FINAL REPORT

HYDROCARBON SAMPLING METHODS

FOR

SOURCE SAMPLING

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Contract No. A7-124-30

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DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

ACKNOWLEDGEMENTS

CONCLUSIONS

1. The use of the ARB version of the Beckman Total Hydrocarbon Analyzer as a source monitor must be done around the calibration curve shown in Figure 5. This figure illustrates saturaticn of the flame ionization detector when fed concentrations greater than about five percent equivalent propane. The curve also shows that precision of measurement is better by a factor of eight in the range of zero to five percent propane than it is in the range of ten to seventy percent.

2. Two methods of sample dilution are available to give usable samples to the measuring instrument:

   a. Dynamic dilution - a continuous system with an estimated precision of the order of ten percent.

   b. Volumetric dilution - a cyclic system operating at one dilution per minute with a precision one percent.

3. An alternative system of oxidizing hydrocarbon to carbon dioxide and then measuring this with a non-dispersive infrared analyzer is practical. It, too, requires a diluted sample.

4. A system of taking "grab" samples in a small bomb has been developed. These samples may be taken from the source itself, or from a sample line. Samples are subsequently diluted and may be given to either measuring system used in this investigation.

RECOMMENDATIONS

As with many investigations that depart from established methods and techniques, the results often generate more questions than anticipated. In this project we believe that the practicality of a dilution system for field measurements as well as a means for the procuring and analyzing of "grab" samples has been established.

These conclusions must still be compatible to the requirements of the California ARB source monitoring program. If our conclusions offer the ARB practical methods for them to achieve their requirements, it is recommended that the dynamic and/or cyclic dilution systems, as described, be assembled for field evaluation. This (these) in conjunction with the existing ARB Model 402, or preferably, a CO_2IR system could provide a 'real world' evaluation of the proposed techniques.

In conjunction with the above, the described "grab" sample technique should be incorporated into the evaluation. This would also provide means to establish the quantitative analysis, periodically, of emissions during a continuous field sampling and analysis run.

Since the oven and related components employed in this study as defined during contract negotiations become the property of ARB, these could form the nucleus of the proposed field evaluation system together with the ARB's existing test equipment.

INTRODUCTION

The scope of work was divided into three distinct segments:

1. The basic calibration of the heated Flame Ionization Detector (FID) Hydrocarbon Analyzer (Beckman Model 402).

2. The response of the FID to an array of hydrocarbon blends consisting of saturates, unsaturates, and aromatics;

3. And attempt to establish the best sampling and detection techniques to assure accurate analysis regardless of hydrocarbon type and regardless of varying composition, viscosity and specific gravity.

One of the primary objectives of this study was to include, wherever possible, a parallel measurement of the test hydrocarbons by catalytically combusting the hydrocarbons to CO_2 with the subsequent analysis of the CO_2 by means of a non-dispersive infrared analyzer (Beckman Model 865).

To assure that comparable results could be achieved, both the FID and CO_2 IR were first subjected to the following hydrocarbon gas blends (in air):

1. CH_4 through C_7H_{16}

2. C_2H_4, C_3H_6

3. C_6H_6

These gases were at $\pm60\%$ of their respective L.E.L.s (from 3.75% to about 0.75%).

Since it was established that very good correlation was achieved comparing the two detection techniques, the program was focused toward similar analyses but starting with pure hydrocarbons followed by appropriate dilution. Such diluted gas streams were then routed to the two different emthods of analysis. It was at this point that the extreme importance of proper sample handling and adequate dilution became overwhelmingly evident. Although the sample injection (via a multi-port GC sample valve) and subsequent dilution was performed within a heated constant-temperature enclosure, results were typically erratic and consistently low, particularly with the FID. By the insertion of a 50 milliliter dilution syringe to initially receive the hydrocarbon sample from the slider valve, results were better but continued to be lower than predicted.

Attempts to calibrate the FID 402 with propane clearly illustrated the problem of dropoff of conversion efficiency as propane concentration increased. At sample flow of 2 cc/minute lessening response started at about 5% propane. Only by lowering the sample flow to 0.3 cc/minute were we able to obtain linear response in the 0-20% propane range. Above 20% response again dropped off.

Since it was established that a typical field sampling condition would involve a mixed hydrocarbon concentration of up to 75%, balance air, and a head-space temperature up to 100°C, the remaining efforts were focused on a test program to provide systems for both continuous sampling and dilution plus a grab sample technique for obtaining such concentration levels.

The following sections describe in detail the systems used for the above efforts and the subsequent tests employed for the high concentration studies.

DESIGN

Four basic designs were used to meet the three principal objectives of this investigation:

1. A dynamic dilution system to generate concentrations of propane in air from zero to one hundred percent (See Figure 1). This system was used to develop response curves for the two measurement systems involved.

    Industrial grade propane and "Zero Air" (contining less than one part per million hydrocarbon) were mixed to generate standards from ten to ninety percent propane in ten percent increments. Each gas was pressure regulated and the flow controlled with a throttling valve before going to its flowmeter. Each flowmeter was calibrated with the gas to be metered using a bubble flowmeter. Pressure, temperature, and water vapor corrections were applied.

2. A simple manifold system (Figure 2) which allowed sampling of standard cylinder gases at ambient pressure. This system was used to sample hydrocarbons at a level of less than four percent in air to determine detector response to various hydrocarbons.

    Two sources of cylinder gases were used. The initial effort was with blends prepared by a nationally known and respected manufacturer. Of the eight blends used, four fit the curve expected, while four were random. Additional blends were prepared in the Beckman facilities, all of which fit the expected curve. Beckman blends were used as the basis of this report.

3. A sample inject system which allowed a one microliter sample of liquid, or a one milliliter sample of vapor (Figure 3) to be diluted with air. This diluted pure hydrocarbons to the linear range of measurement for the ARB instrument, again to determine how the detector responded to different compounds.

    The first effort injected a one milliliter aliquot of propane vapor into a flowing stream of zero air. Giving this to a mixing chamber resulted in an exponential dilution which made peak height measurements difficult to reproduce.
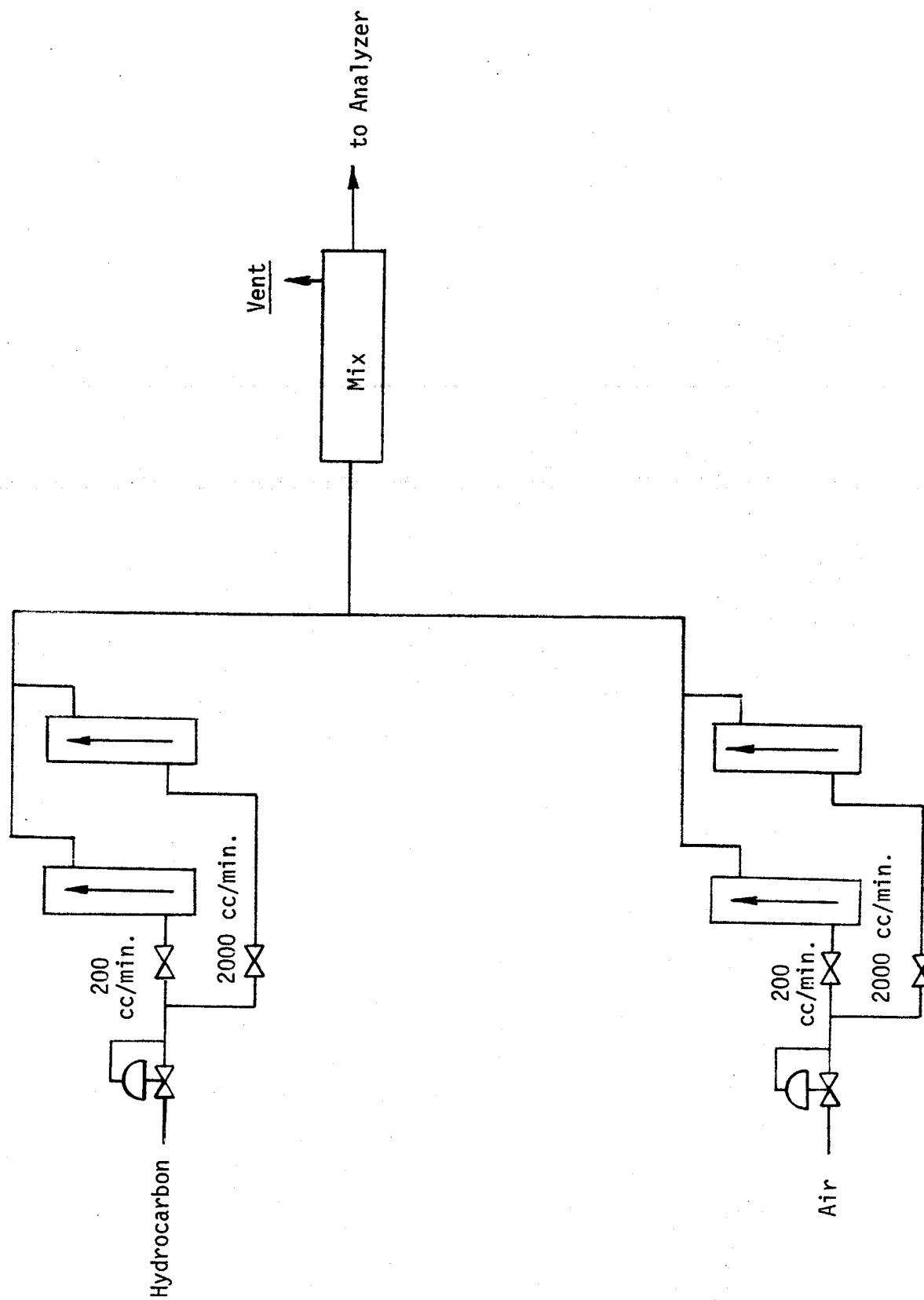
FIGURE 1.

DYNAMIC DILUTION SYSTEM

FIGURE 2
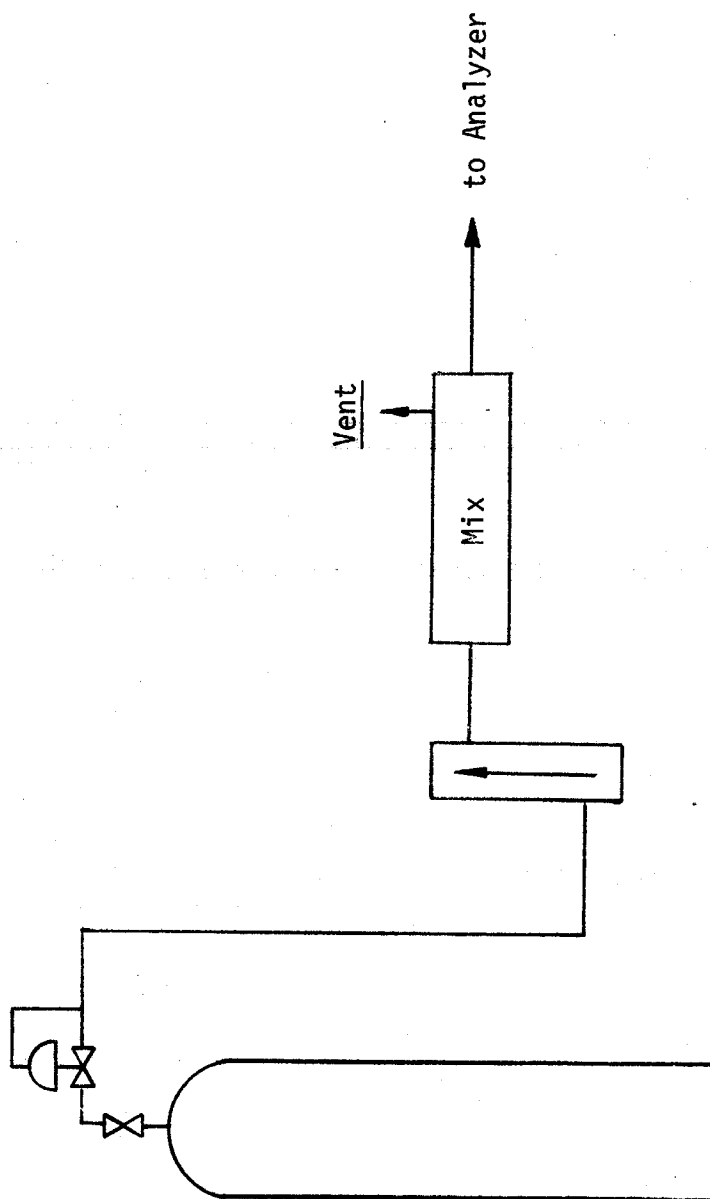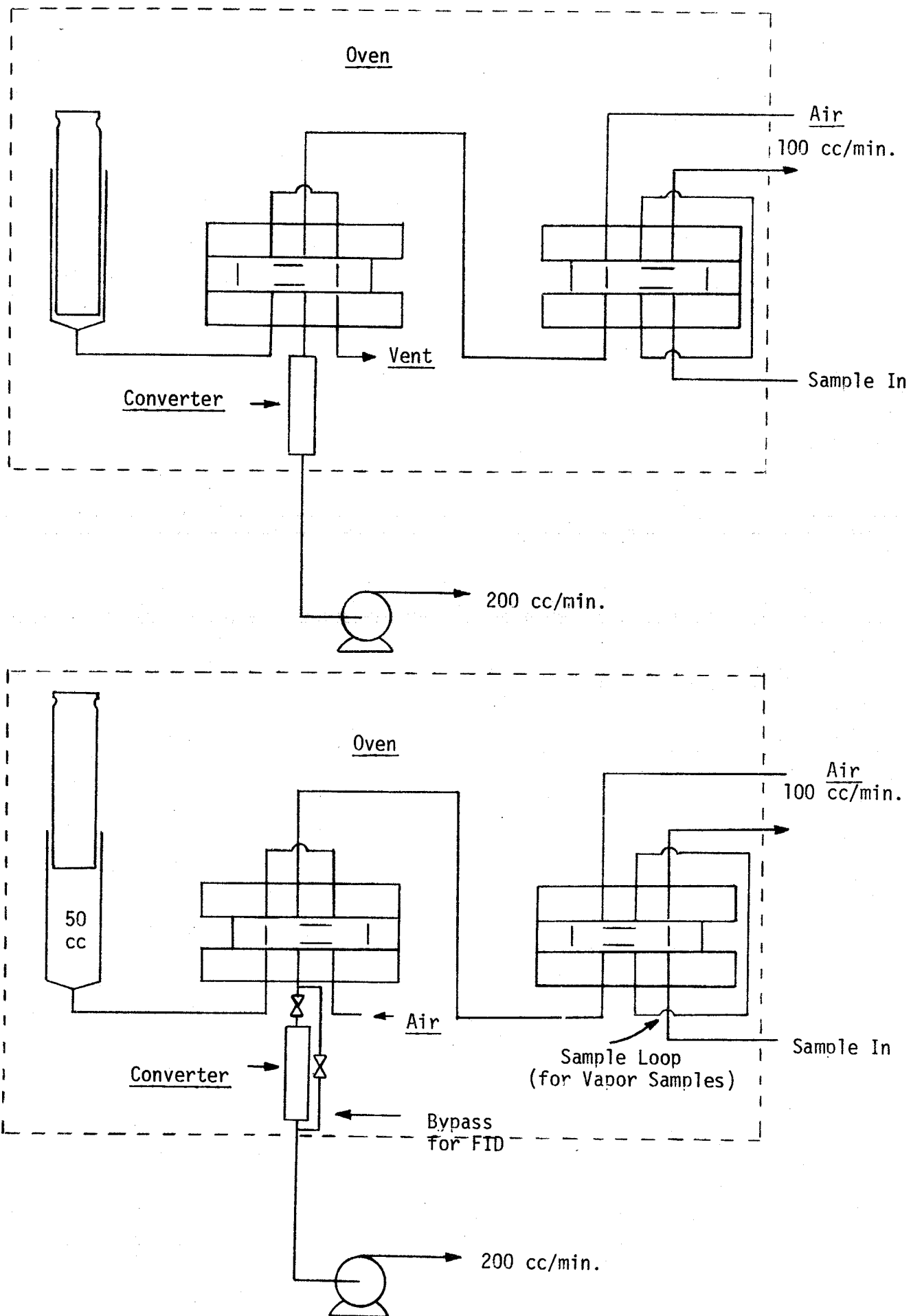
SIMPLE MANIFOLD SYSTEM

Oven

Air
100 cc/min.

Vent

Converter

Sample In

200 cc/min.

Oven

Air
100 cc/min.

50 cc

Air

Converter

Sample Loop
(for Vapor Samples)

Sample In

Bypass
for FID

200 cc/min.

FIGURE 3 - SYRINGE INJECTION SYSTEM

A variation of this system was to inject into a syringe, follow with zero air to dilute to fifty milliliters, and then withdraw this dilution to the measuring systems. Reproducibility was excellent for any one concentration, but linearity was marginal.

4. A system to allow taking of a grab-sample. This allowed a high concentration of hydrocarbons, such as from the head space of a tank, to be sampled, diluted and then measured by a standard instrument.

This system employed a 100 cc sampling cylinder fitted with valves at each end. The cylinder was evacuated and taken to the sampling point. Any lines connecting the cylinder to the sampling point were purged with sample, the cylinder valve opened, and the pressure of cylinder and sample allowed to come to equilibrium. When this was done, the cylinder valve was closed.

If the temperature of the vapors being sampled was higher than the temperature of the cylinder, condensate formed in the cylinder. To get a reproducible volume of sample the 100 cc cylinder was put into an oven maintained at 150°C (see Figure 4). This cylinder was connected to a second evacuated cylinder of four liter volume, but blocked from it by valves. The free end of the sample cylinder was vented by way of a flexible tube to a cup of water, the tube dipping beneath the surface. The vent valve was held open until no bubbles issued from the vent tube. Now the vent valve was closed and the valves between the two cylinders opened. The vent line was removed and zero air fed to the free end of the sample cylinder until pressure in both cylinders was equalized to ambient. This operation resulted in a constant volume of sample being diluted with zero air to insure that any sample withdrawn from the cylinders ahd a dewpoint below ambient temperatures.

With the original sample now safe to handle at ambient temperature, the cylinders were purged with forty liters of air and the effluent collected in a Tedlar bag. The bag was kneaded to ensure mixing, and then used as a source for the measuring systems.

EVALUATION

1. The standard instrument used by the Air Resources Board for source monitoring of hydrocarbons is the Beckman Model 402 Total Hydrocarbon Analyzer fitted with a long capillary. This capillary allows 2 cc per minute of air to be fed to the flame ionization detector at a head pressure of 4 psig. Figure 5 shows the response of this instrument to concentrations of propane varying from zero to seventy percent. The response is clearly non-linear beyond approximately five percent propane.

In source monitoring of crude oil storage tanks, the ARB must measure up to 75% hydrocarbons typically. The composition of these tank overheads is generally unknown. It must be expected that the range of carbon numbers will vary widely, depending on how long the mixture has been held and the temperature of the tank. A test was devised to determine flame ionization detector response to mixtures of C_6, C_7, C_8, C_9, and C_{10} in propane in approximation of the mixtures expected.

A mixture of air and propane is sparged through a liquid hydrocarbon kept at a constant temperature in a bath. The effluent is maintained at a ratio of 75% hydrocarbon/25% air by adjusting propane flow to keep oxygen content at 5%. When the system has reached equilibrium, the mixture is analyzed with the Model 402. (See Appendix for calculations).

The table following lists test conditions and results. The scale readings of the test are in relation to calibrating the Model 402 with a 75% propane/25% air mixture and spanning to 75% of scale. To show a fit on the calibration curve of Figure 5, these scale readings were recalculated for a curve developed with a mixture of 50% propane/50% air and spanning for 50% of scale.

Test HC	t^oC	Mixture Air	Mixture C_3H_8	HC	C_3H_8	Span @ 75% Scale	Span @ 50% Replot
C_3H_8	----	25	75	---	75	75	61.5
C_6H_{14}	17.4	25	61.7	13.35	88.5	83	68.1
C_7H_{16}	43.0	25	60.3	14.7	94.6	85	69.7
$i-C_8H_{18}$	46.1	25	57.8	17.2	103.7	87	71.3
C_9H_{20}	40.2	25	73.6	1.4	77.8	77	63.1
$C_{10}H_{22}$	38.5	25	74.5	0.52	76.2	77	63.1

Replacing the long capillary with a shorter one of smaller diameter allowed a feed of 0.32 cc per minute to the flame at a head pressure of 0.25 psig. The response curve for the same instrument with this lower feed is now linear to twenty percent propane (Figure 6).

14.

Samples of hydrocarbons to be prepared per system described in previous report whereby 25% air plus 75% mixtures of propane plus heavier hydrocarbons are blended and admitted into evacuated sample cylinder

Controlled
Constant Temperature Oven

100 cc

4000 cc

FID (402)

CO₂ IR

CAT. CONV.

Cylinder
Dilution Air

Tedlar Bag
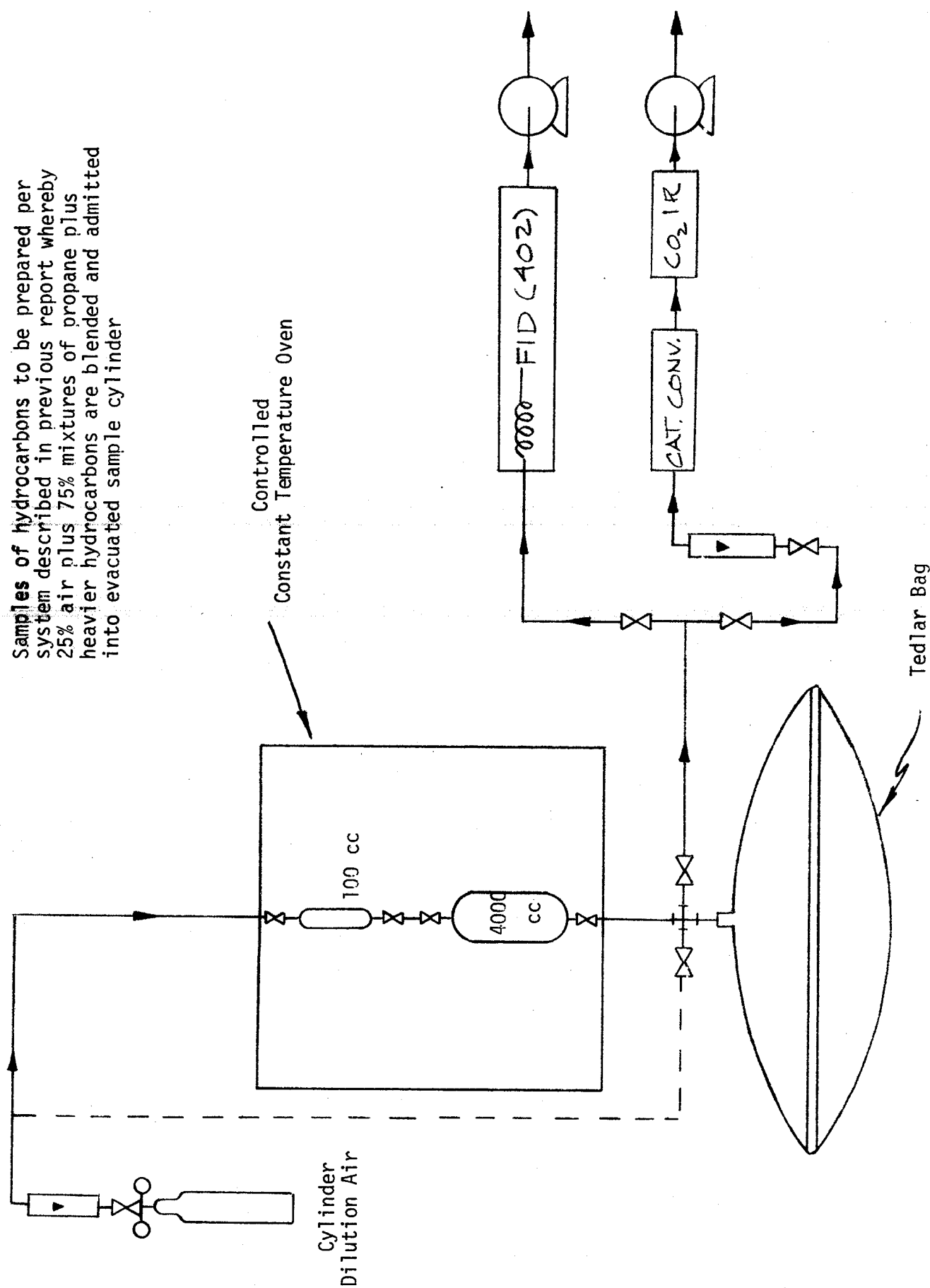
FIGURE 4.
GRAB SAMPLE DILUTION/TRANSFER SYSTEM

FIGURE 5

CALIBRATION OF THE 402 FID VS PROPANE AND
WITH 75% HYDROCARBON MIXTURES IN
PROPANE

16.

% PROPANE IN AIR

BECKMAN MODEL 402 FID
FLOW TO FLAME 0.32 CC/MIN.
1/4 PSIG 40:60 H₂/He TO
FLAME @ 100 CC/MIN.
350 CC/MIN. AIR TO FLAME
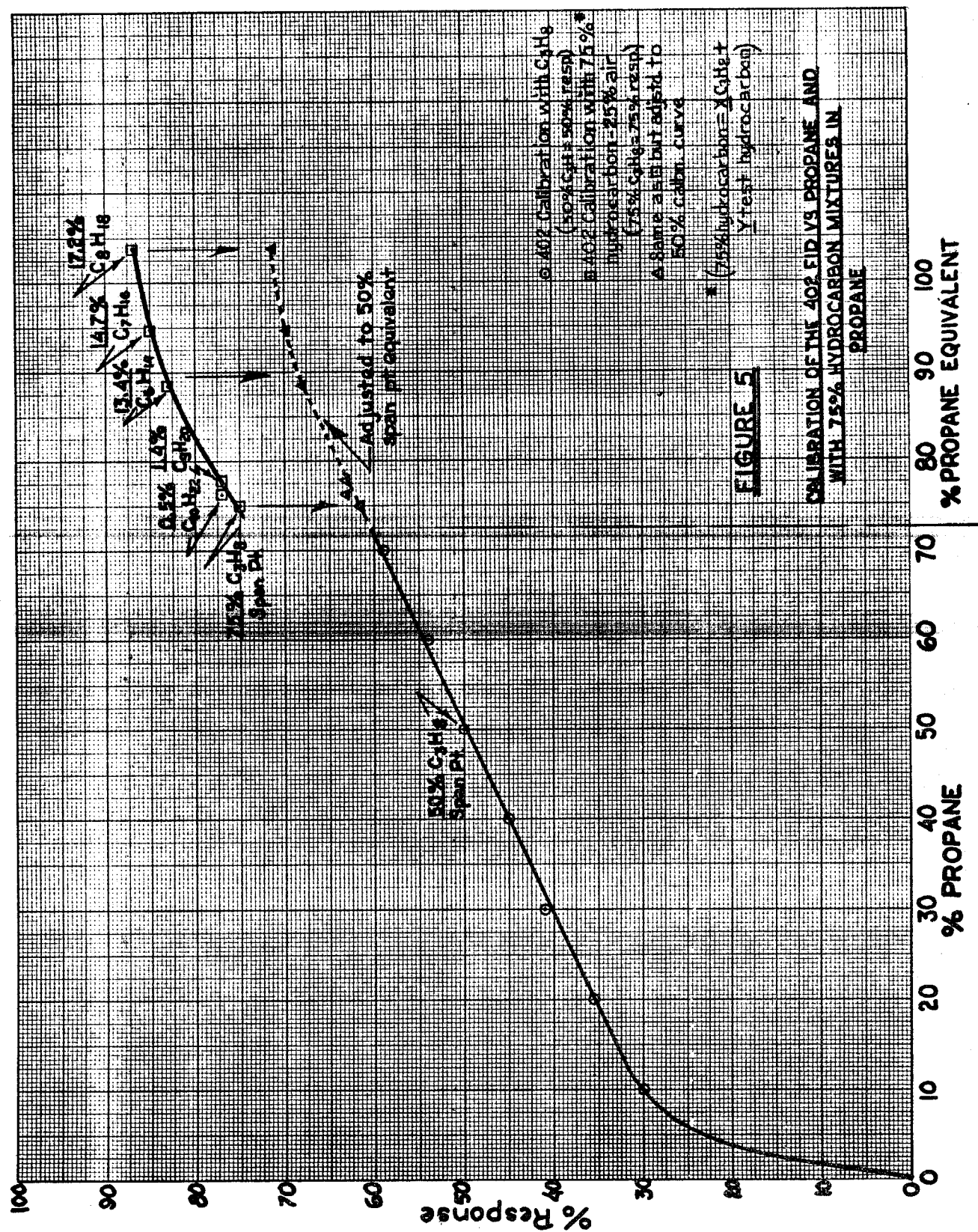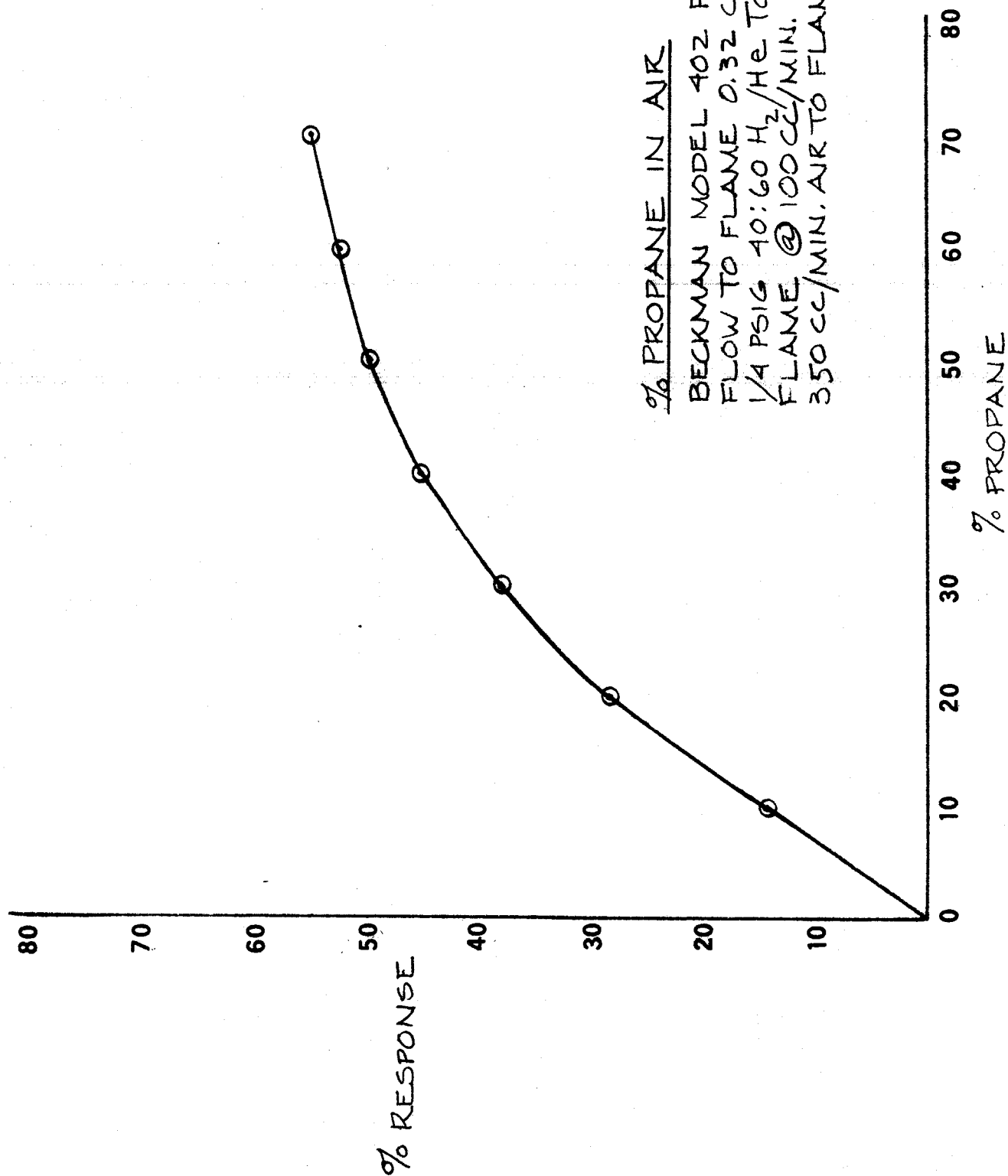
It is obvious that the flame ionization detector becomes saturated when the level of propane fed to the flame reaches 0.1 mol percent. Inasmuch as it is not practical to restrict the feed of sample to the flame to less than 1 cc per minute, the only alternative is to make a source dilution of the sample to prevent concentrations greater than an equivalent of ten percent propane from being sampled. Figure 7 shows linearity of the detector feeding 1 cc per minute to the flame while sampling from zero to ten percent propane.

2. An alternative approach to measure hydrocarbons in air is oxidation to carbon dioxide and measuring with a non-dispersive infrared analyzer. The system employed in this investigation was a catalyst bed of palladium on alumina held at 500°C for oxidation and a Beckman Model 865 Non-Dispersive Infrared Analyzer to measure carbon dioxide.

This system also requires sample dilution. For one volume of propane to be oxidized, twenty-five volumes of air are required; for one volume of octane, 62.5 volumes of air. The combustion approach, however, does have the advantage of always measuring the same component (carbon dioxide) and thus eliminates the problem associated with the flame ionization detector of relative response to different compounds. Figure 8 shows a comparison of these two measurement systems analyzing the source samples of methane. Figure 9 compares the response of these two systems to one mol percent samples of three different hydrocarbons.

Two methods of source dilution were considered:

3. A continuous dilution at the sample probe. This would involve metering a zero air to the probe as a diluent. To meter sample flow directly presents the problem of contending with varying temperatures and viscosities from point to point. These effects can be minimized by measuring total flow through the sample tube. That is, if 2000 cc per minute of zero air is given to the probe and 2100 cc per minute is metered through the sample line, 100 cc per minute of sample is being diluted by a factor of twenty to one. The sketch of such a system (Figure 10) illustrates the two-stage dilution system in further detail.

4. Cyclic dilutions, described above, which involve taking a discrete sample at timed intervals, diluting it in a heated chamber and giving this dilution to the measuring instrument. The principal disadvantage to this method is that the volumes prepared are too low to be used by the Model 402 Total Hydrocarbon Analyzer, so the investigation was restricted to catalytic oxidation of the sample and then measuring CO_2 by infrared.

This method makes dilutions with great precision (see Figure 11). The curve superimposed on the chart of Figure 11 shows an exagerated Beer Lambert curve believed to be the result of inaccuracies in the blends given to the system. It does appear to hold the most promise for a reliable system for source monitoring.

The cyclic rate is a function of flow rates. Using a 50 cc dilution, a carrier flow of 100 cc per minute and an exhaust flow of 200 cc per minute, a forty-five second cycle is used. This appears to be a good compromise between speed of response and precision of dilution.
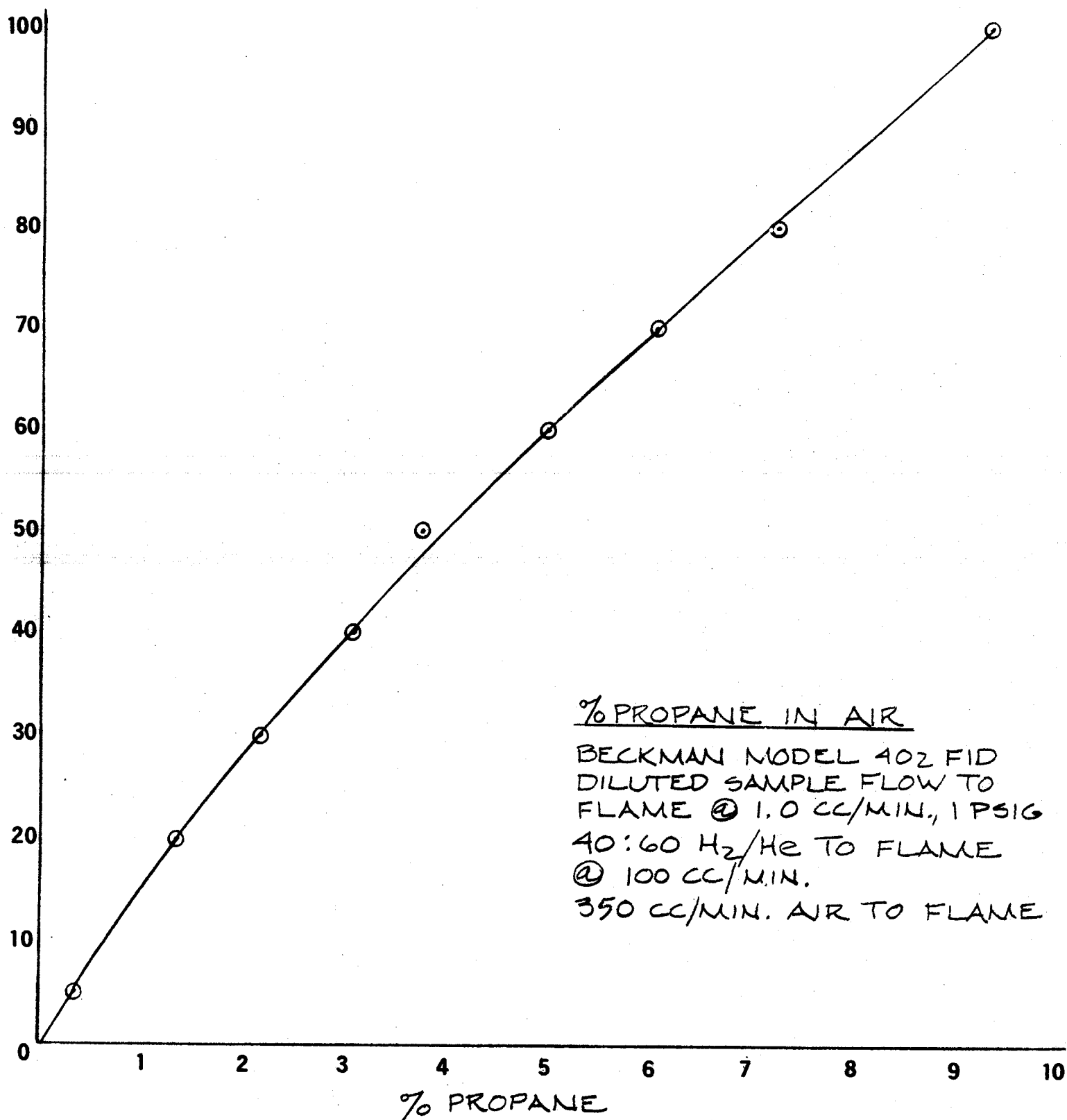
% PROPANE IN AIR

BECKMAN MODEL 402 FID
DILUTED SAMPLE FLOW TO
FLAME @ 1.0 CC/MIN., 1 PSIG
40:60 H_2/He TO FLAME
@ 100 CC/MIN.
350 CC/MIN. AIR TO FLAME

% PROPANE

FIGURE 7.
MODEL 402 DILUTED CALIBRATION - 1.0 CC/MIN.

CALIB. & COMPARISON OF FID vs CO_2IR

NOTE: SL. CURVATURE OF CO_2IR
CURVE TYPICAL BEER'S
LAW EFFECT
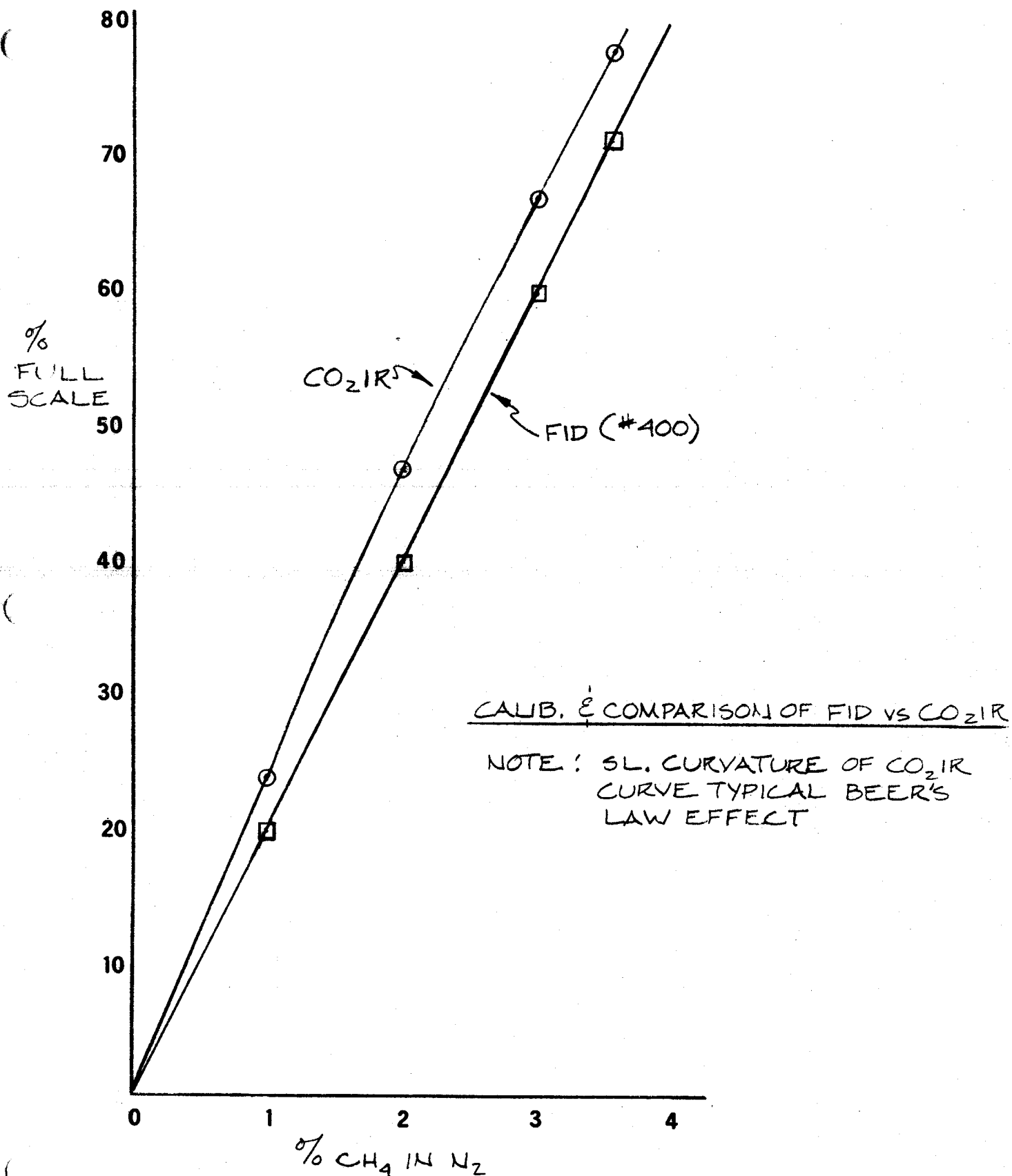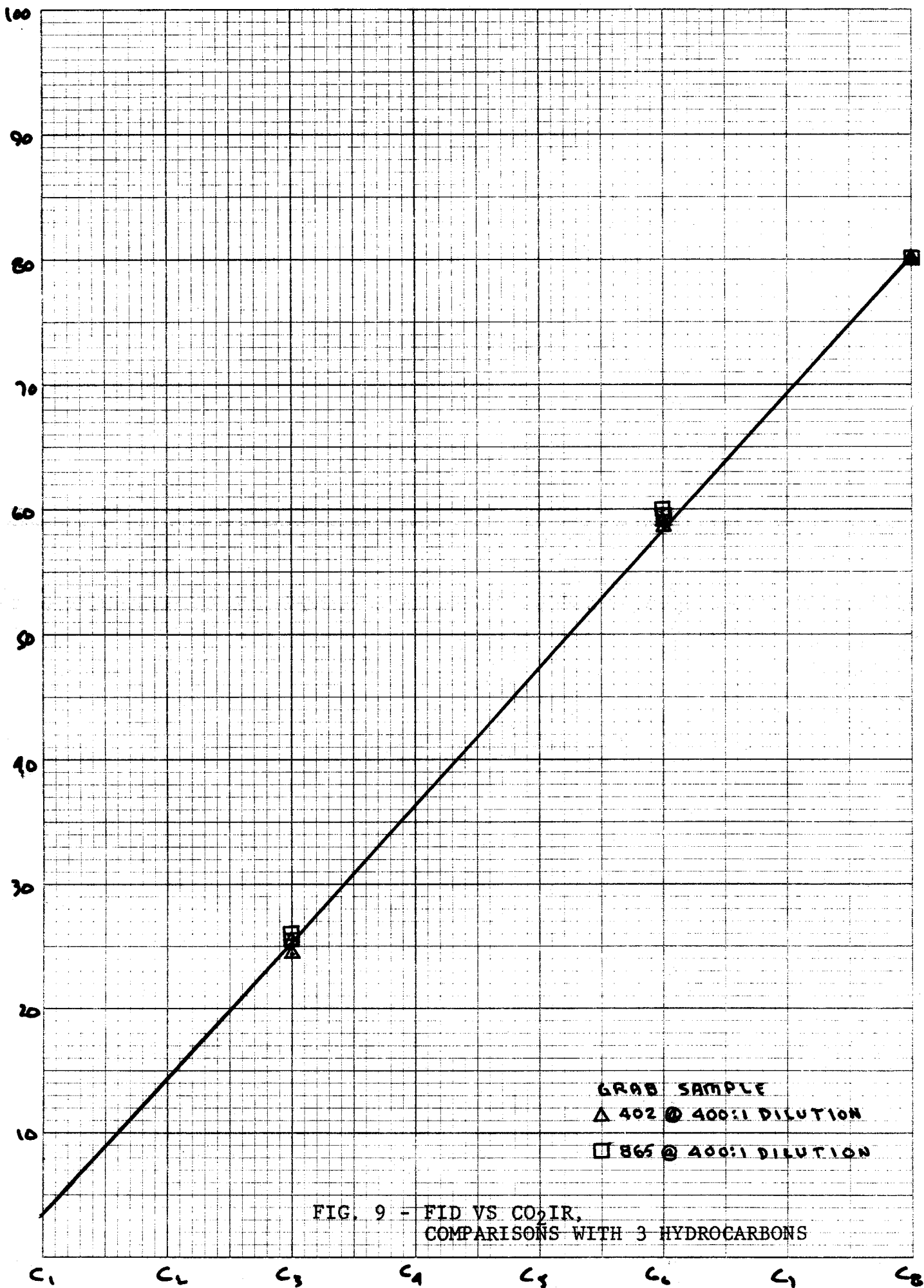
FIGURE 8.
FID VS. CO_2 IR, CALIBRATION WITH METHANE

46 0780

10 X 10 TO THE INCH.• 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

GRAB SAMPLE
△ 402 @ 400:1 DILUTION
□ 865 @ 400:1 DILUTION

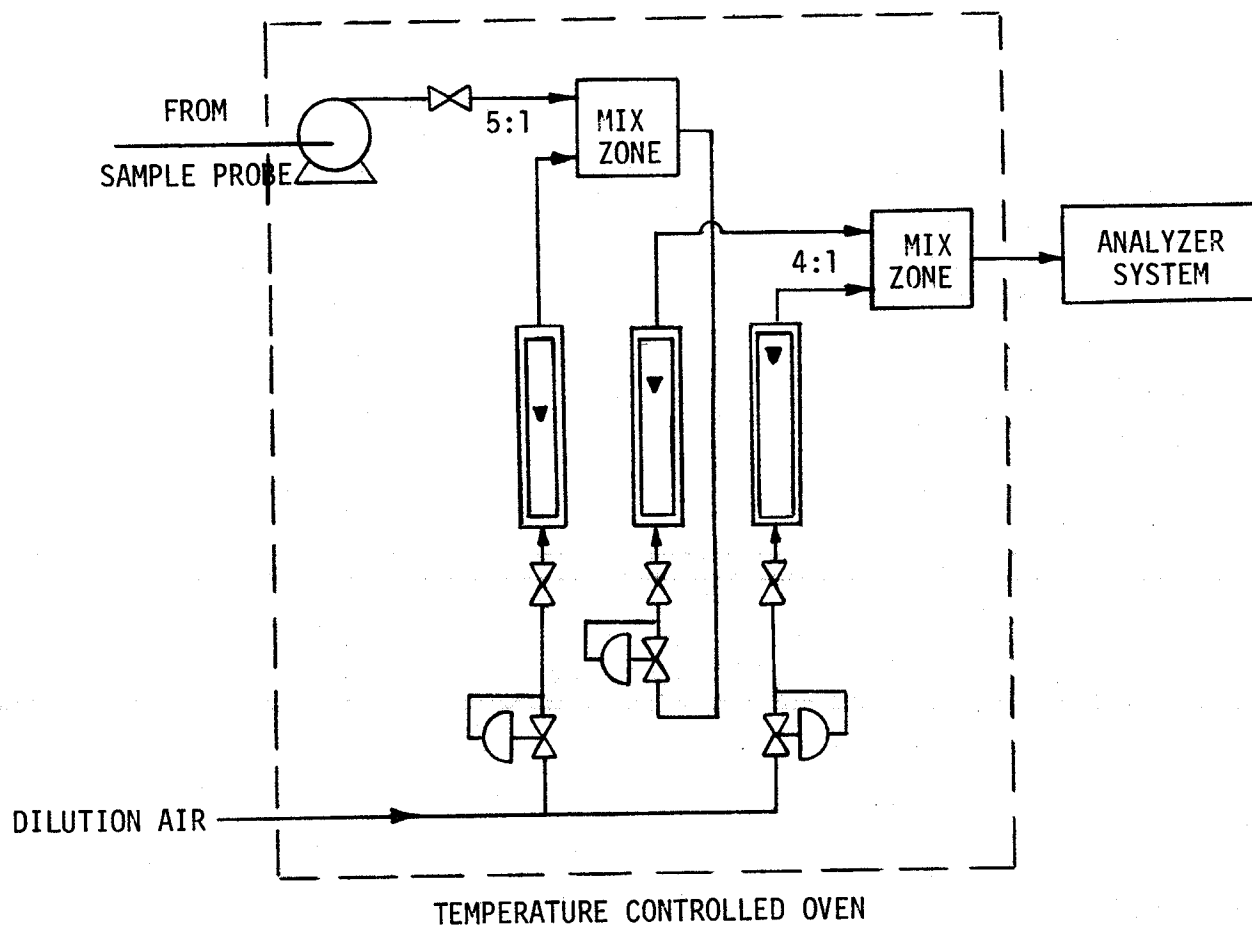FIG. 9 - FID VS CO_2 IR,
COMPARISONS WITH 3 HYDROCARBONS
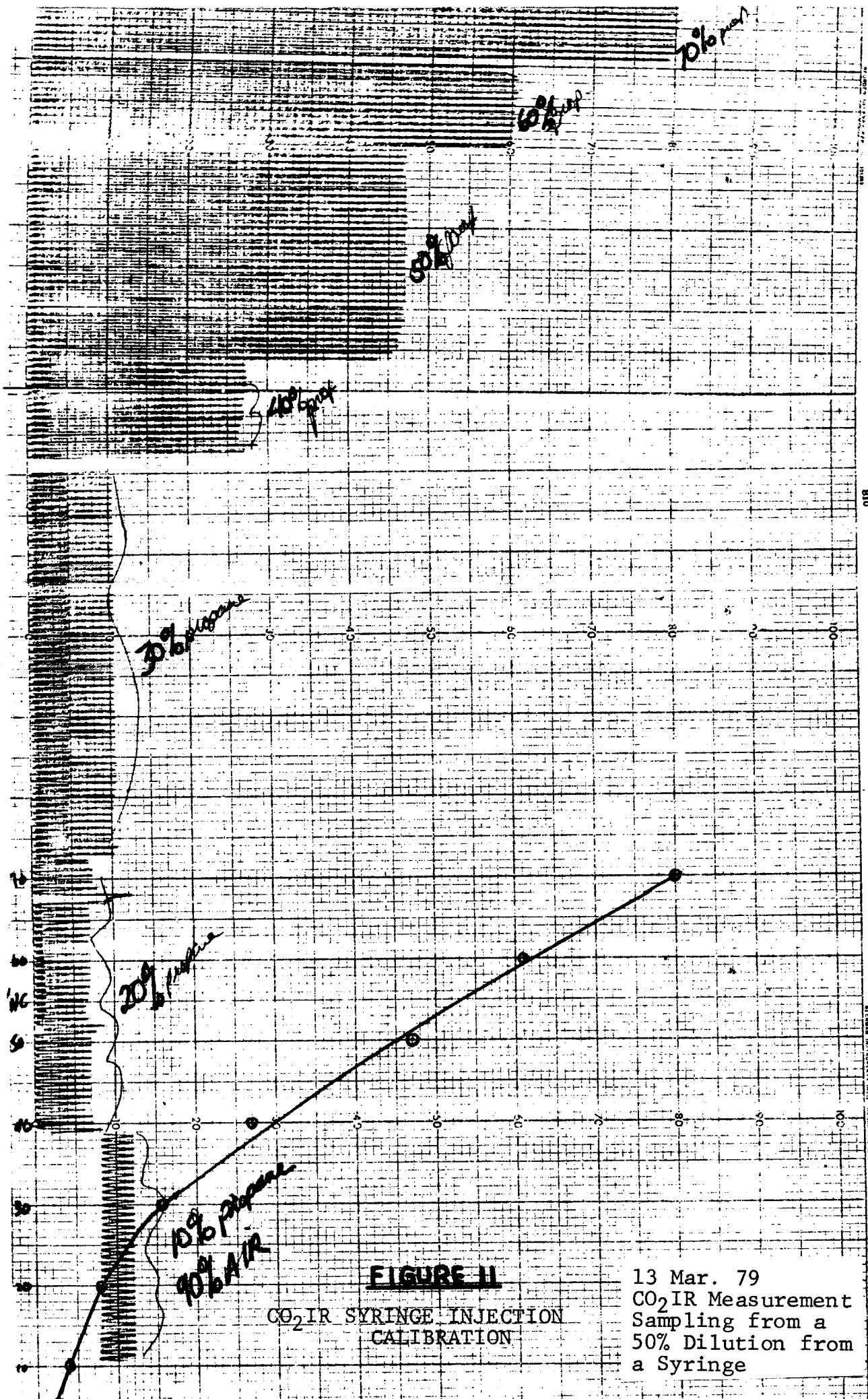
FIGURE 10.

CONTINUOUS 2-STAGE DILUTION SYSTEM

FIGURE 11

CO₂IR SYRINGE INJECTION CALIBRATION

13 Mar. 79
CO_2 IR Measurement
Sampling from a
50% Dilution from
a Syringe

5. The "grab sampling" system was used to evaluate both the flame ioni-
    zation detector and the catalytic combustion infrared measuring tech-
    niques. Inasmuch as linearity of both of these systems with respect
    to concentration had already been demonstrated, this part of the
    demonstration was restricted to system response to constant volumes
    of pure hydrocarbon vapor. Each test was done in duplicate, using
    propane, hexane, and iso-octane.

    The procedure followed was to evacuate both bombs with a high-vacuum
    pump, introduce sample, bring up to temperature, equilibrate the
    sample bomb with ambient pressure, release sample bomb to the larger
    bomb, equilibrate, and purge both bombs with forty liters of air into
    a Tedlar bag. After kneading the bag to insure an homogeneous
    sample, it was sampled with the Model 402 Total Hydrocarbon Analyzer.
    The bypass of the Model 402 was used to feed the infrared system. The
    comparison of these two systems is shown on the previously referenced
    Figure 4.

DISCUSSION

The following discussion will first consider the dynamic sampling and analysis.
The subject of grab sampling techniques will be treated separately in the
second segment of this section.

Since the ultimate objective of this study is to provide a more accurate
means of accessing the hydrocarbon emissions at point sources, such as at
crude oil storage tanks, the following aspects must be considered:

1. Accuracy of measurement

2. Simplicity of measurement

3. Reliability of measurement

1. Accuracy of Measurement - Since one of the primary objectives of this
    study was to compare the pros and cons of the FID versus the CO_2 IR
    approach, this should be the first consideration to be discussed. Let
    us itemize the attributes and limitation of both analytical techniques.

    The FID Hydrocarbon Analyzer

    Attributes: A. High sensitivity, it can measure accurately to
                       and including the part per billion levels (PPB).

                   B. It produces an accurate linear output from the
                       PPB to the low % levels.

                   C. It measures continuously and with minimal attention.

    Limitations: A. When analyzing unknown mixtures of hydrocarbons, the
                       response factors will vary which directly affects
                       the accuracy of the measurement.

B. When the air/oxygen background of the sample varies, the "oxygen synergism" effect will impact upon the accuracy of the analysis.

C. Use of capillaries to restrict flow, which in turn is aimed at permitting higher % level hydrocarbon measurements, causes unknown variability of flow rate to changing viscosities of the unknown hydrocarbon mixture. This also impacts upon the accuracy of the measurement.

D. At least two cylinder gases are required.

The CO_2 IR Analyzer - This analyzer actually is an analytical system consisting of a standard non-dispersive infrared analyzer sensitized to measure CO_2 preceded by a catalytic combustion zone. This zone typically consists of a quartz tube filled with a catalyst, such as palladium, on a ceramic or asbestos substrate. The tube is surrounded by a heating mantle and the temperature is typically maintained at 500-600°C. No evidence of catalytic conversion deficiency has been found to date. It was originally planned to use a cobalt oxide catalyst and operate at 950°C since this has been widely tested and employed to convert hydrocarbons to CO_2 in organics in wastewater applications. For this purpose no organic compound has been found to date that does not convert with 100% efficiency. However, the former approach (palladium at 500°C) was selected since the temperature requirements are much less demanding looking ahead to some semi-portable system for use in the field. Regardless, the higher temperature cobalt catalyst approach is available should future shortcomings be found using the palladium.

Attributes:
A. Rugged, widely employed for many years for ambient, source, and automotive pollution monitoring networks. Measurement parameters include CO, SO_2, NO_x and total hydrocarbons (as hexane).

B. Probably has the best on-line performance record of any stream analyzer.

C. Lends itself readily to auto zero/auto cal. calibration systems often supplied with the IR analyzers.

D. In measuring CO_2 essentially no interferences or variable responses are encountered.

Limitations:
A. Cannot reach the PPB levels. Typical minimum range is 0-50 ppm, $\pm 1\%/24$ hours reproducibility.

B. Depending upon concentrations being measured, the output is not strictly linear but follows Beer's law.

Both analytical techniques suffer a common limitation - neither can measure hydrocarbon concentrations much in excess of $\pm 5\%$ total carbon concentration*. With this seemingly unalterable conclusion, it becomes

*This is not a maximum limitation for the IR in normal applications not involving preliminary catalytic conversion to CO_2.

obvious that a pre-dilution step must be integrated into any field analysis procedure when it is anticipated that a double-digit hydrocarbon atmosphere is to be measured.   With that fact in mind, the decision must be made as to the selection of the best analytical technique - FID versus CO_2 IR.   Once it is recognized that an approximate 20:1 dilution must be incorporated into the measurement system, the dilemma of unknown viscosity influences are drastically reduced - also oxygen synergism. However, the FID response factor variations remain despite the dilution effect.   Contrarily, the CO_2 IR remains free of such problems.   This aspect, coupled with the simplicity and freedom from peripheral gases and maintenance requirements, tends to make the CO_2 IR the most attractive option.

2.   Simplicity of the Measurement - If it is accepted that the CO_2 IR analysis is the optimum measurement technique, the key to successful future field measurements of source hydrocarbons will be the simplicity and dependability of the total system.

At present, the California State Air Resources Board employs a 100-foot heated sample probe that is capable of withdrawing a headspace, or venting sample of a hydrocarbon mixture from the top of a tank, such as crude oil storage tank, to ground level.   Such a sample is pulled from its source by means of a pump downstream of the FID 402 analyzer.

In order to interject a precise dilution which, for the sake of discussion, will be assumed to be a 20:1 dilution, at least two options are available.

A.   Dynamic continuous dilution - Since the flow of the sample gas from the source may require maintaining temperatures to $100^{\circ}C$ and the hydrocarbon concentration may range from low level to 100%, the use of flow measuring and controlling devices becomes tedious, of questionable accuracy, and certainly not simple.   Again, the problems of viscosity and density must also be recognized.

Thus it is our recommendation that, if a truly continuous sampling system is required (contrary to the following Part B in this section), a dynamic flow measurement and control of the dilution gas and the combined diluted sample gas flow be accomplished.   Again, assuming a 20:1 dilution of the gas to be analyzed, the dilution required should be done in cascade.   It will be noted from Figure 12 that metered flow of propane and air mixtures changes by a factor of two over the actual flow in going from pure air to pure propane. To suppress this effect, a preliminary dilution of five to one is done. This ratio is selected as a compromise between the viscosity effect demanding a large ratio and the dilution error demanding a small ratio. A final dilution of four to one will bring total dilution error of about eleven percent with a dilution of 20:1.

B.   Intermittent sample dilution - As described earlier under Methods of Source Dilution, highly accurate dilutions can be achieved by employing volumetric sample and dilution technique. By the use of a slider valve, a precise volume of sample can be measured and dispensed. This sample

GAS FLOW vs % PROPANE IN AIR
(ROTAMETER @ CONSTANT 100 CC/MIN.)

CURVE CORRD. FOR H₂O VAPOR IN SOAP BUBBLE CALBN.
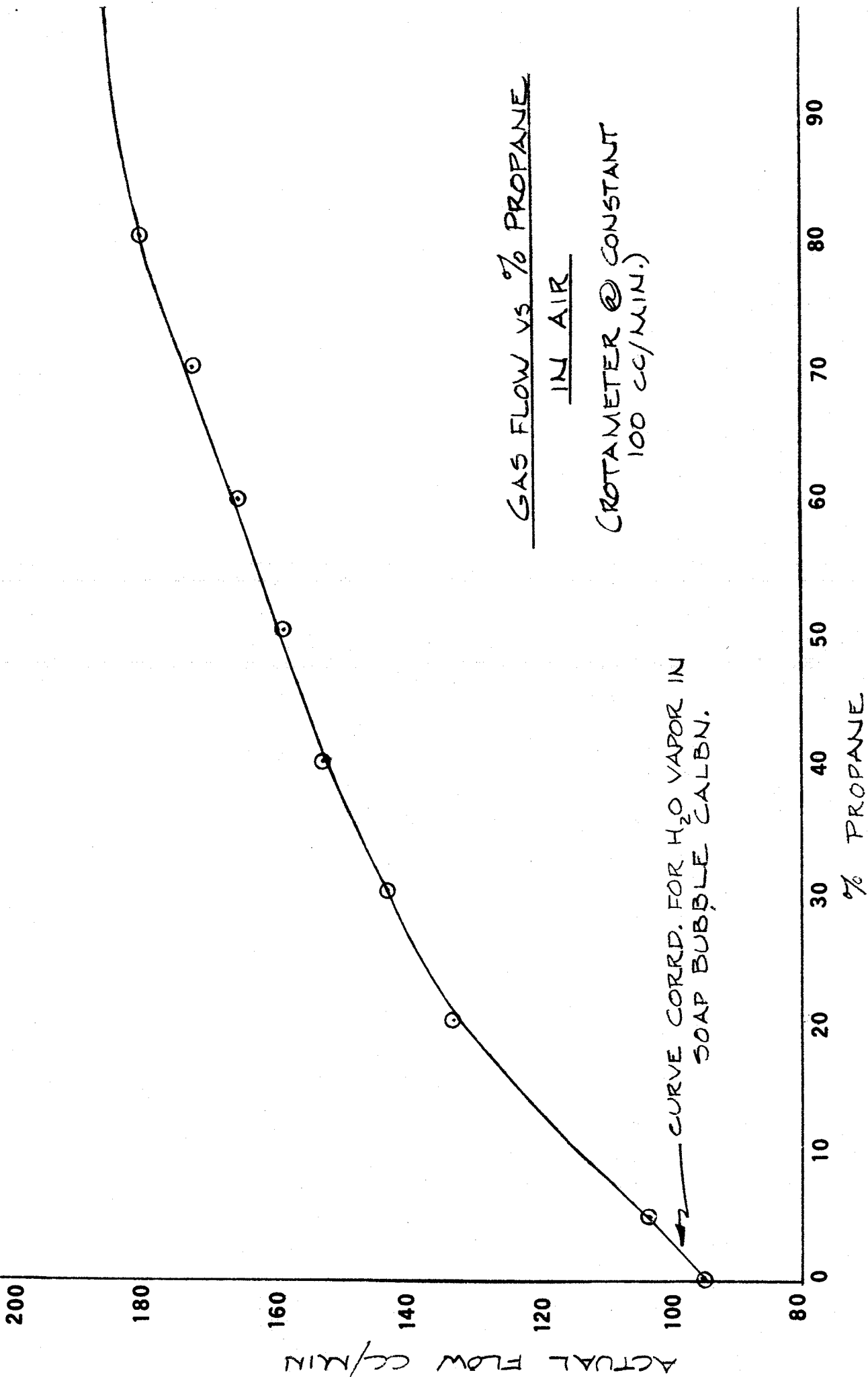
% PROPANE

ACTUAL FLOW CC/MIN

FIGURE 12.

GAS FLOW VS. VARYING PROPANE

can be contained within the valve itself or, for larger samples, be contained in a sample loop into and out of the slider valve. Since this sample must be contained and diluted, at least initially, within an elevated temperature zone to avoid any condensation, a heated chamber must also be included in this scheme. Also, a programmable timer must be inluded to actuate the cycle. This cycle can be repeated on a once per minute timing. This may still not be acceptable to the Air Resources Board since we have been advised verbally that a continuous measurement is desired. The concentration levels should appear as a series of peaks whose heights should correspond to prevailing concentrations.

From a simplicity standpoint in comparing the two above options, the continuous technique must be the simplest but at the sacrifice of the accuracy we know can be achieved in the intermittent method. To bolster the accuracy of the continuous method to the level of the intermittent method, we suspect that the desired simplicity would be lost. We believe that the combination of precise, calibrated rotameters coupled with high sensitivity pressure differential flow controllers on both the dilution gas and combined diluted hydrocarbon gas will result in a known sample gas stream whose volume will be known to about 10% accuracy. Presumably, this would provide an acceptable total system accuracy. If not acceptable, the volumetric intermittent technique is recommended.

3. Dependability of the Measurement - Dependability of the measurement system encompasses a number of critical segments; the primary sample probe and transmission, the dilution control system and the analytical system. Inputs from the ARB staff indicate that time spans for on-site measurements are about 24-48 continuous hours. If this is correct, it is believed that all segments used in this investigation survive this period with minimal attention following initial calibration. Stability could be further improved by incorporating an off-the-shelf auto zero/auto span module to account for any short term span or zero drift.

Grab Sample Analysis of Source Hydrocarbons

The technique described previously wherein an evacuated cylinder receives a headspace or venting source hydrocarbon sample for subsequent analysis is an obvious and attractive method of sampling. However, the technique to reliably transfer and dilute the sample prior to analysis has a number of potential pitfalls and opportunitites for error.

The results obtained during this project, although not refined to the extent desired, were very promising. Once a large, heated, evacuated cylinder was employed downstream from the heated sample cylinder, the problems of condensation and subsequent revolatizing were eliminated. The evacuated sample cylinder (100 ml) must be filled with the desired sample with a minimum dead space between sample source and cylinder inlet. Thus, the sample should flow directly to the cylinder inlet valve prior to admitting sample into the cylinder. Since the cylinder probably will be at a lower temperature than the flowing sample, the sample flow into the cylinder should be stopped when pressure equilibrium is reached. This should prevent the partitioning of heavies within the cylinder due to condensation.

Once the sample cylinder is heated to a temperature above the original sample and the excess pressure vented as described earlier, a known volume sample is available for subsequent dilution into the larger evacuated and heated cylinder fol-

lowed by dilution gas to fill a Tedlar bag to an ultimate volume of 40 liters. Once mixed within the bag, a 400:1 diluted sample is available for analysis by GC, FID, or CO_2 IR.

We believe that this sampling procedure represents a practical means to sample source hydrocarbons. To calibrate the instrument the same technique can be employed as we did during our tests. A slight excess of hexane or octane can be injected into the same type of evacuated cylinder. Once the cylinder is heated to a temperature higher than the boiling point, the cylinder can be vented back to atmospheric pressure and diluted as described.

Recommended Hydrocarbon Monitoring System for Future Field Measurements by the ARB

As suggested in the above discussion, Figure No. 13 attempts to summarize the features of an optimum field monitoring system for source hydrocarbons. The system is based on the assumption that a heated flexible sample probe is available and of such length that the dilution and analysis can be performed at a convenient ground level. The sample will be withdrawn by means of a pump similar to the heated stainless steel bellows pump employed in the Model 402 Hydrocarbon Analyzer. A portion of the discharge is directed to a gas mixing chamber which also receives an accurately measured and controlled flow of dilution air. To eliminate ambient temperature variations, both flow measuring and control systems should be mounted within the common temperature controlled oven (at 100° or greater) together with the pump and mix zone. The analyser system should be close coupled to the oven but external to it.

As mentioned earlier, this system will suffer from the unalterable problem of multiplying by two any flow measurement inaccuracies. Thus, if at least a 20:1 dilution is required, the flow difference which represents the true flow rate of raw sample, will suffer from these cumulative inaccuracies. Thus, it is urged that the intermittent dilution by controlled temperature slider/dilution syringe be given serious consideration as an alternate. Regardless of choice, the accuracy of either analytical system will be a vast improvement compared to the use of the FID 402 directly whenever dealing with high hydrocarbon concentrations.
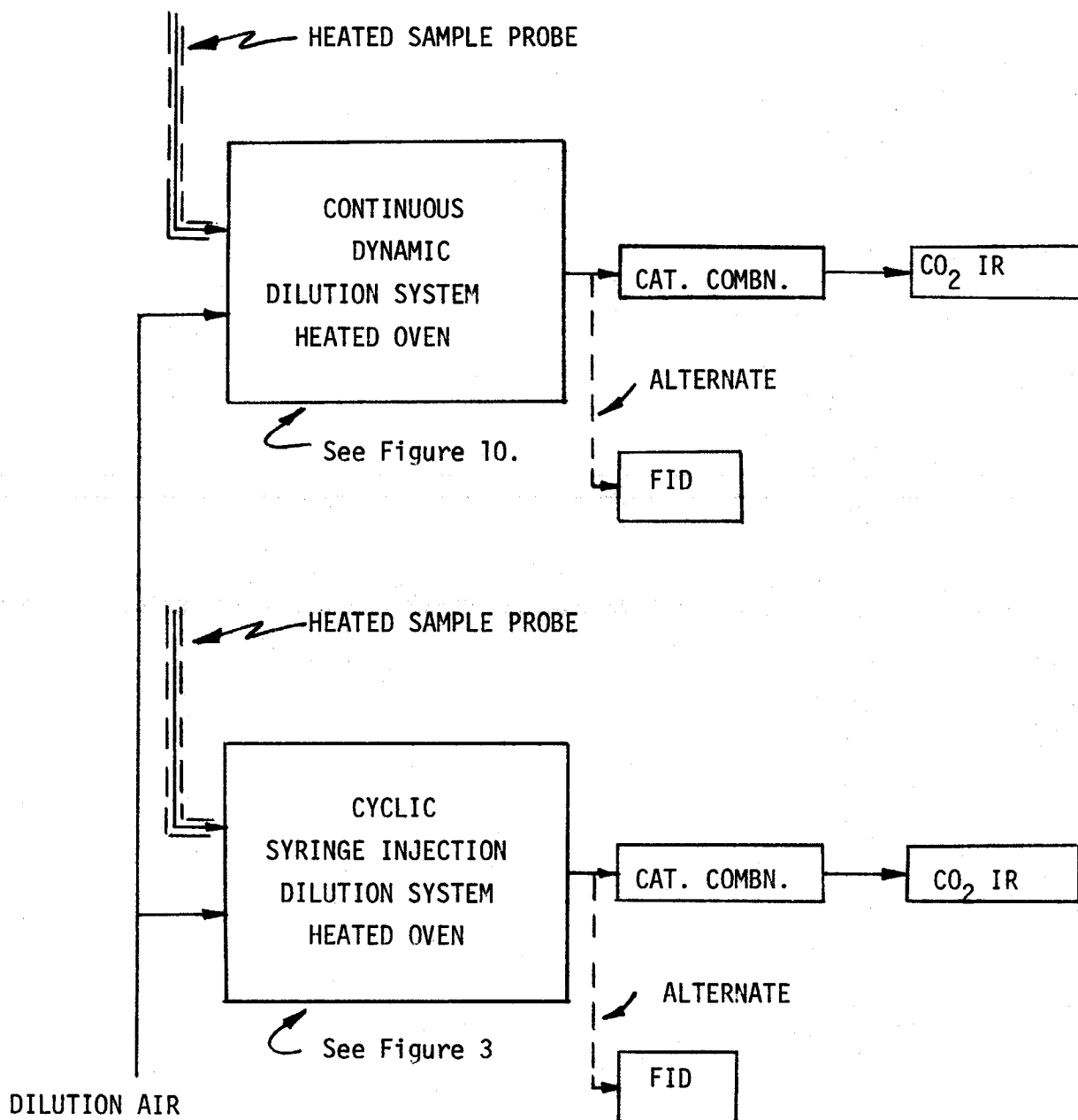
FIGURE 13.
RECOMMENDED FIELD MONITORING SYSTEM(S)

GLOSSARY OF TERMS

CO_2	Carbon Dioxide
CO_2IR	Carbon Dioxide Infrared (analyzer)
FID	Flame Ionization Detector
GC	Gas Chromatograph
IR	Infrared (analyzer)
L.E.L.	Lower Explosive Limit
NDIR	Non-Dispersive Infrared (analyzer)
PPB	Parts per Billion
PPM	Parts per Million
PSIG	Pounds per Square Inch

APPENDIX

This contains a series of calibration curves spanning with 3.58% methane and using an array of +60% L.E.L. hydrocarbon blends to establish equivalent response using the Beckman Model 400 FID.

These calibration curves have been presented in previous contract progress reports and are included here for further information for those who may not have such earlier reports.

LIST OF FIGURES

APPENDIX

FIGURE 14.

1.82% C₂H₆ SAMPLE GAS

ACTUAL 400 READING

CORRECTED 400 READING

CALIBRATION DATA
3.58% CH₄ SPAN
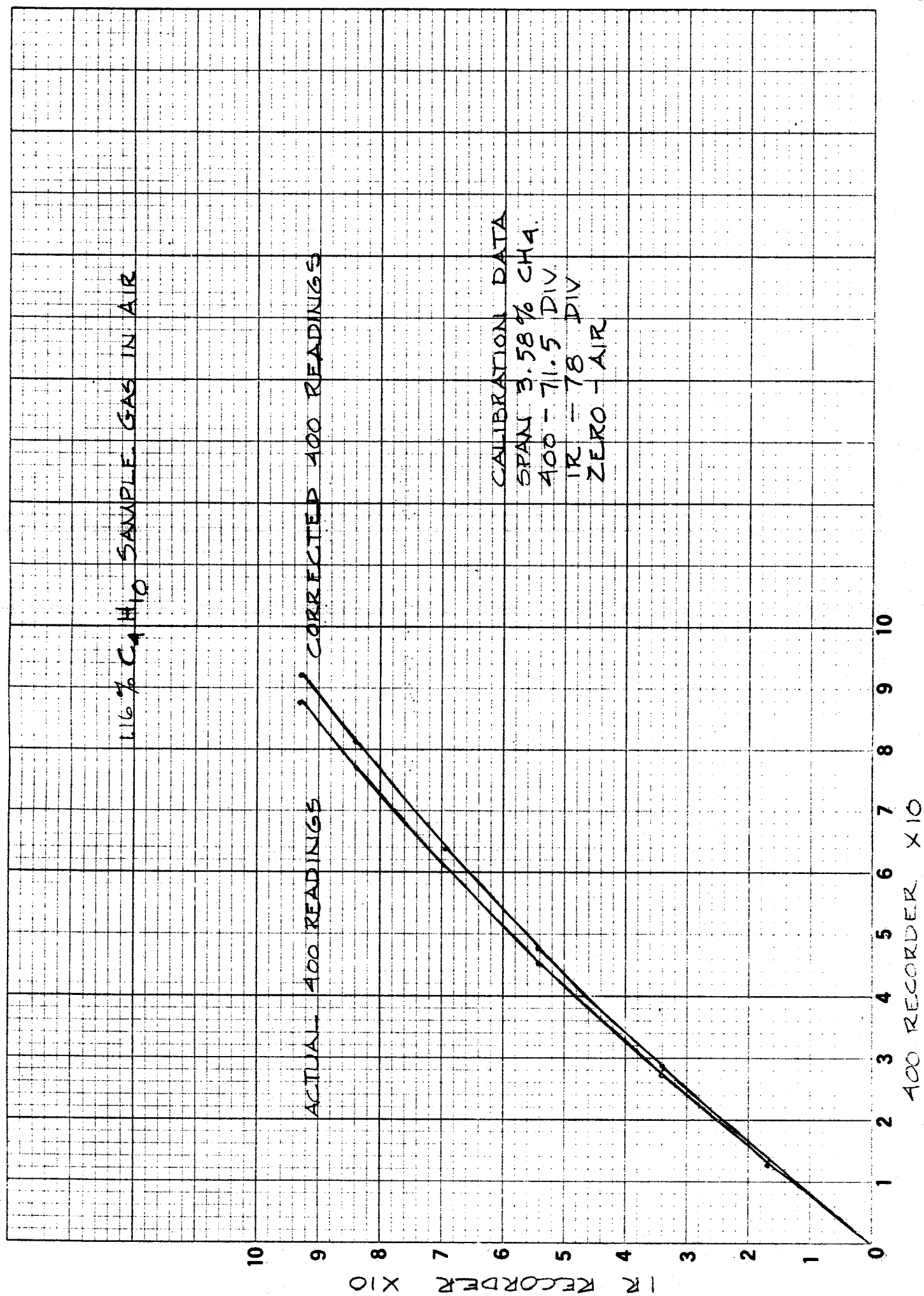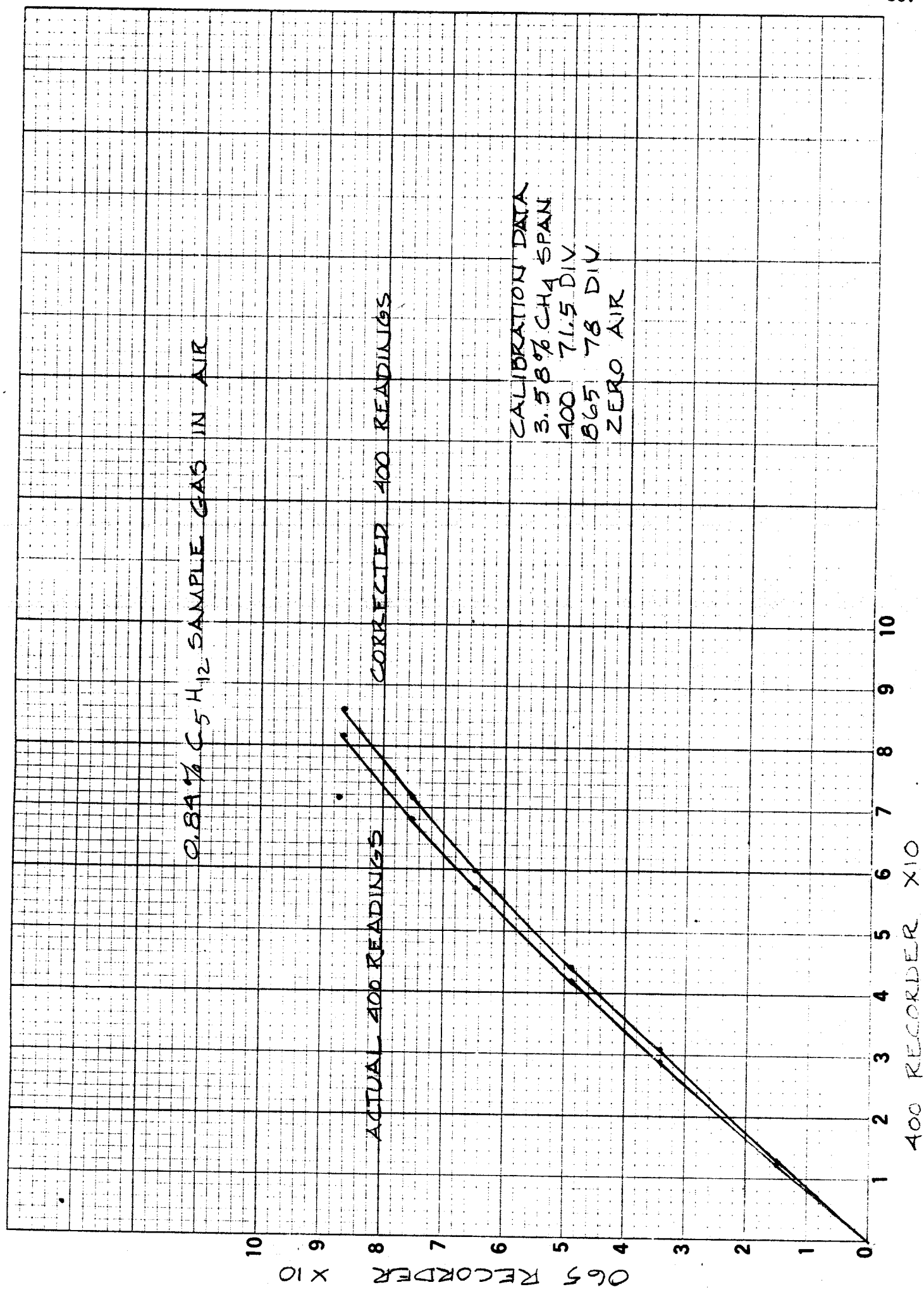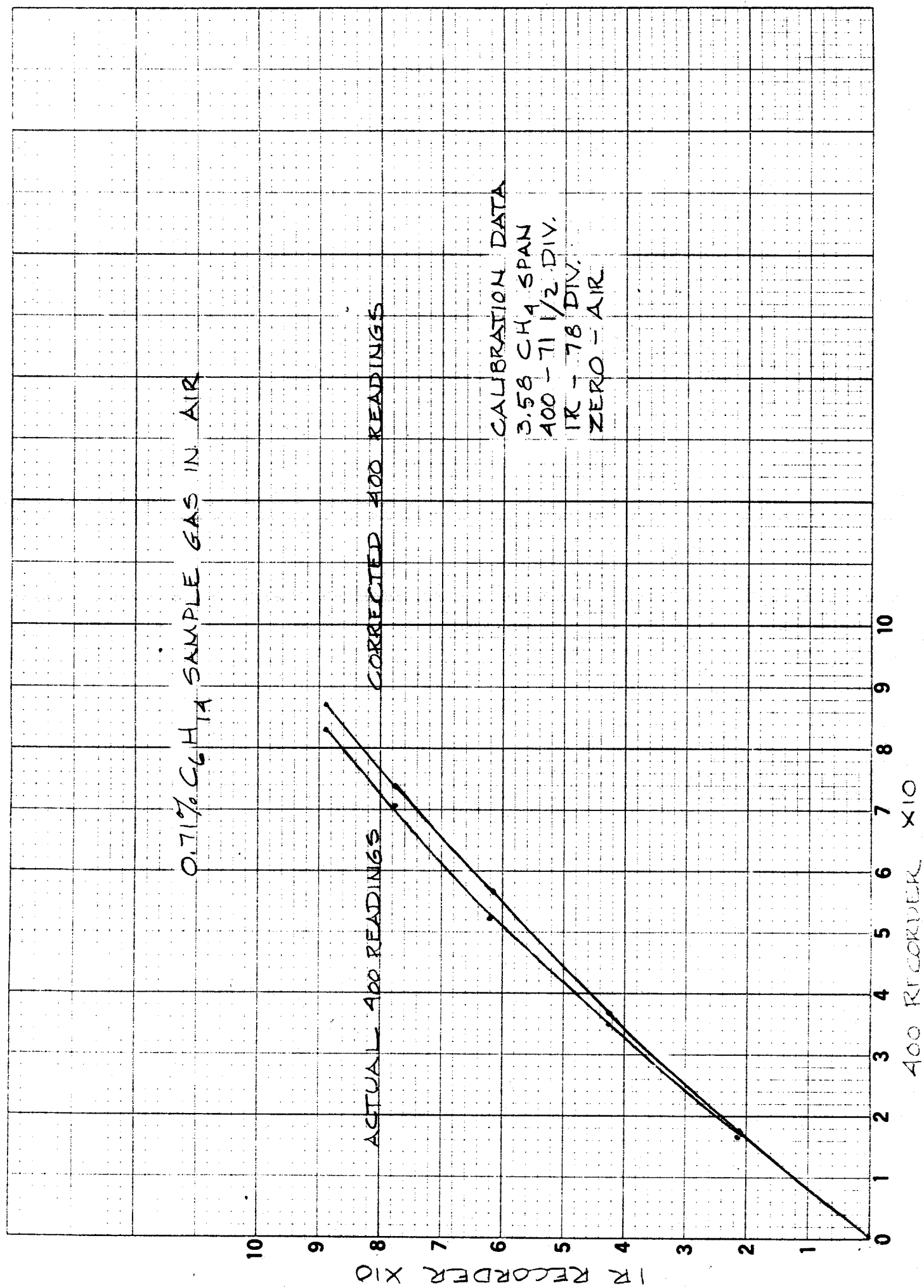400   71½ DIV.
IR   78 DIV.
ZERO AIR

FIGURE 15.

33.

FIGURE 16.

FIGURE 17.

35.

FIGURE 18.

FIGURE 19.

FIGURE 20.

FIGURE 21.

2.38 C₂H₄ SAMPLE GAS

CORRECTED 400 READING

ACTUAL 400 READING

CALIBRATION DATA
3.58% CH₄
400, 71 ½ DIV.
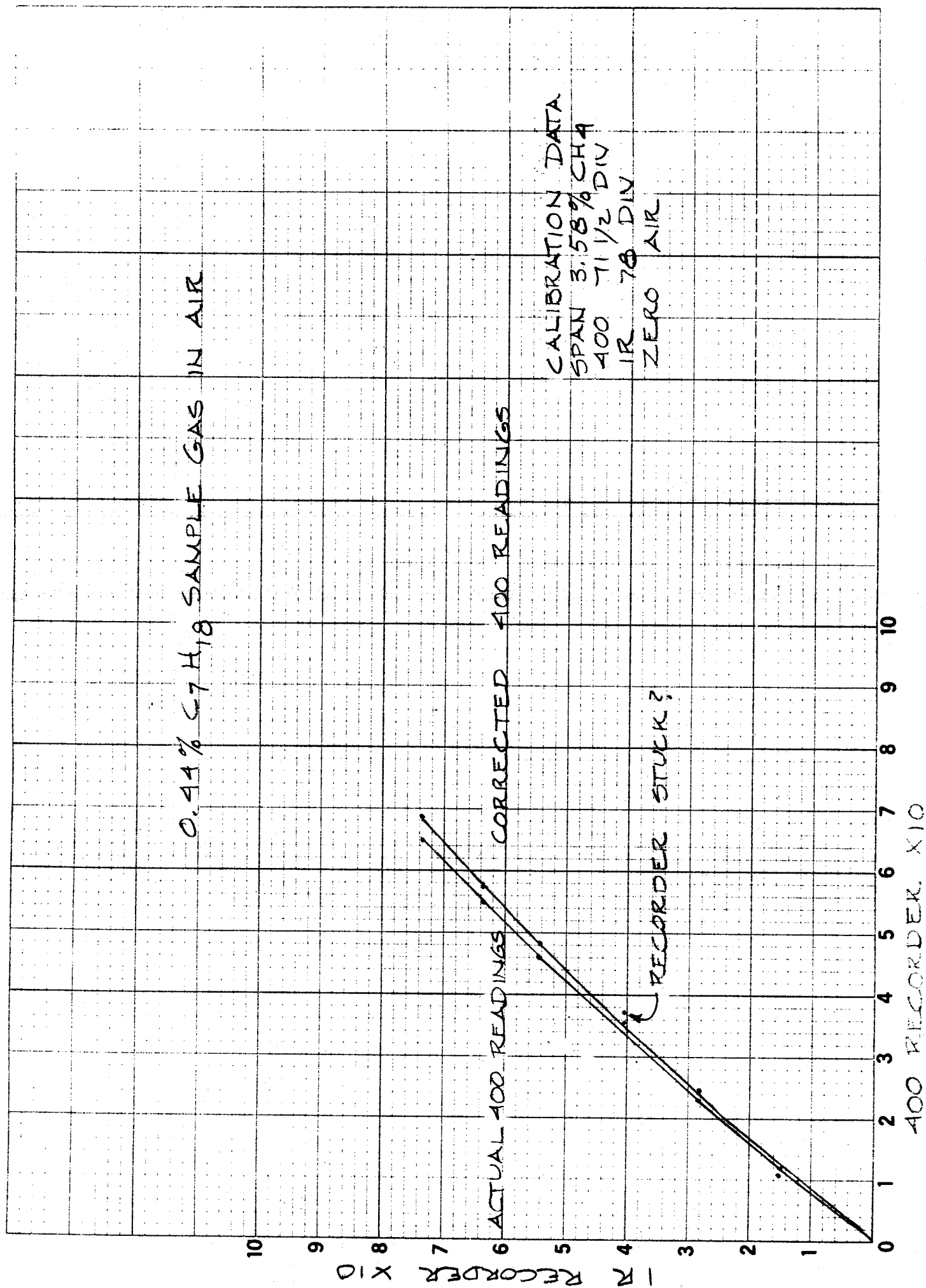IR 78 DIV
ZERO AIR

400 RECORDER X10
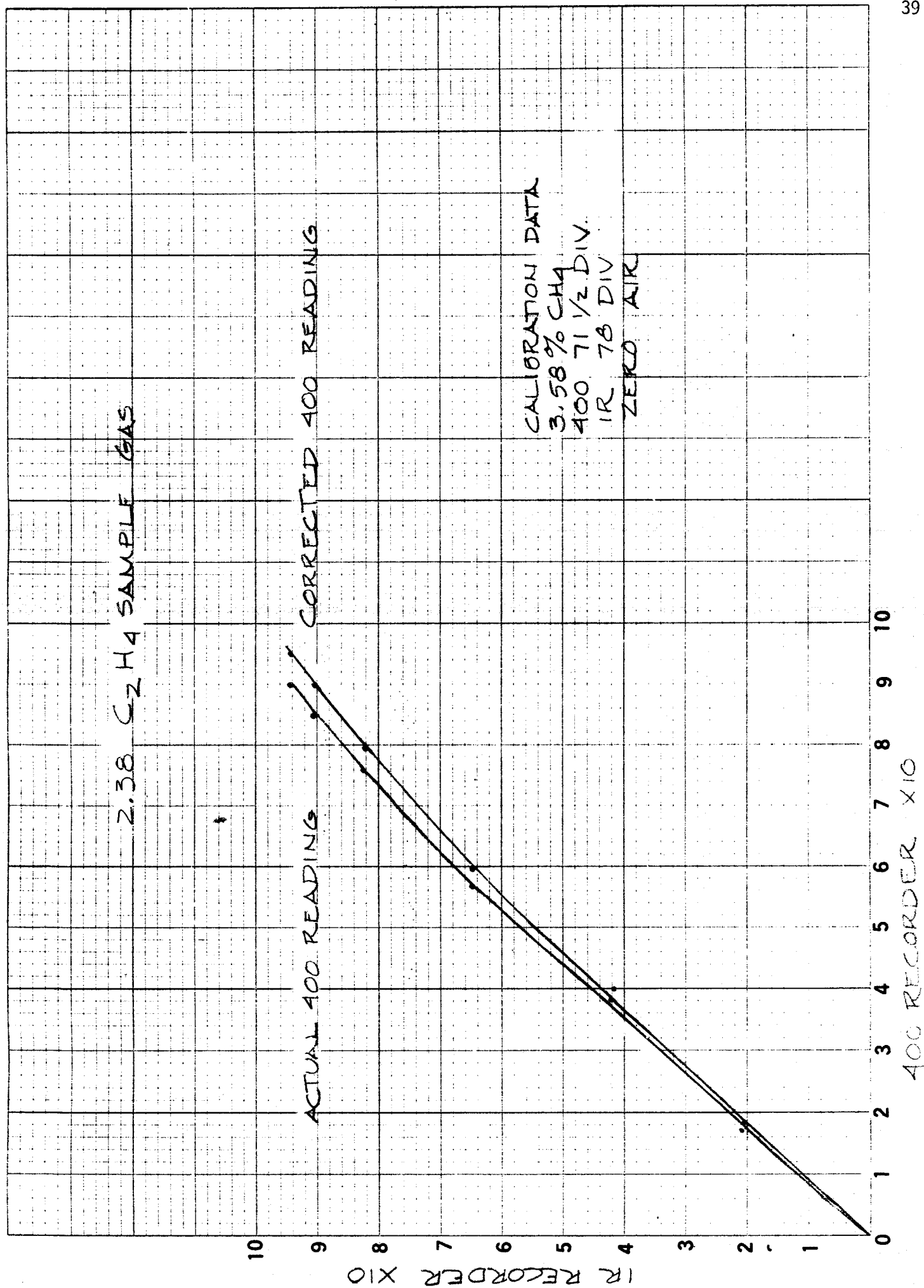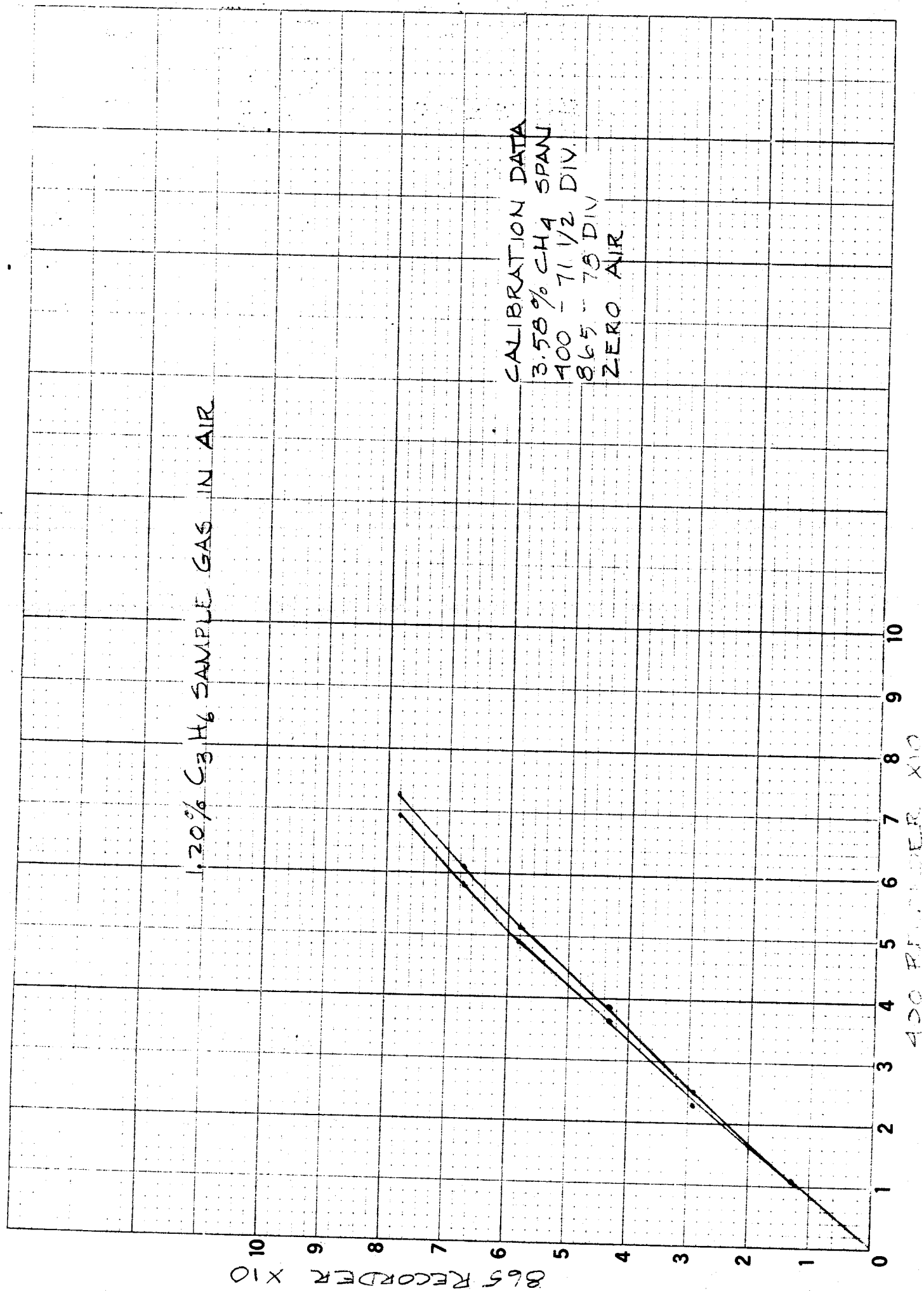
IR RECORDER X10
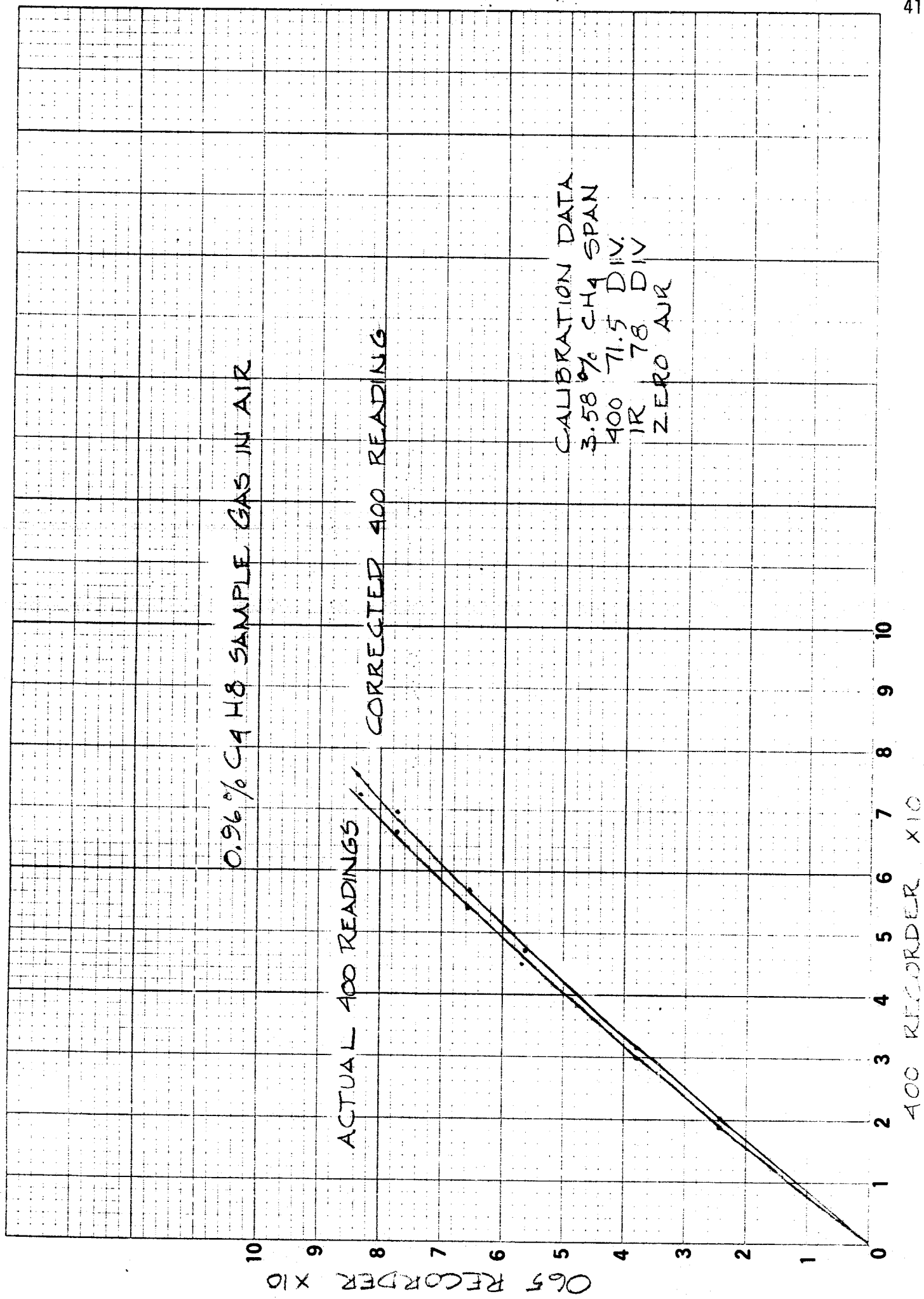
FIGURE 22.

FIGURE 23.

FIGURE 24.

0.84% C_6H_6 SAMPLE GAS IN AIR

CORRECTED 400 READINGS

ACTUAL 400 READINGS

CALIBRATION DATA
3.58% CH_4 SPAN
400   71 1/2 DIV.
IR   78   DIV.
ZERO AIR

400 RECORDER × 10

APPENDIX

An air-propane mixture is sparged through a liquid hydrocarbon at a controlled temperature. The output gas is controlled at five percent oxygen by adjusting propane flow.

What is the distribution of the test hydrocarbon in propane? System pressure is 760 torr.

ASSUMPTION 1. Air is totally insoluble in hydrocarbons.

ASSUMPTION 2. The dynamic mixing of gas and liquid is complete. This allows the use of Raoult's Law, which states:

"Molar weights of non-volatile non-electrolytes when dissolved in a definite weight of a given solvent under the same conditions lower the solvent's freezing point, elevate its boiling point, and reduce its vapor pressure equally for all such solutes."

Where the subscript 3 represents propane and the subscript n represents the test hydrocarbon, Raoult's Law may be written:

$$X_3 P_3^0 = P_3 \tag{1}$$

$$\text{and } X_n P_n^0 = P_n \tag{2}$$

$$\text{given } X_3 + X_n = 1 \tag{3}$$

$$\text{and } P_3 + P_n = P_t \tag{4}$$

where P_t = total pressure = (75%)(1 atmosphere) = 570 torr

To solve for P_n:

$$P_3 = P_t - P_n$$

$$P_3 = P_t - (X_n P_n^0)$$

but $X_n = 1 - X_3$

$$\therefore P_3 = P_t - P_n^0 (1-X_3)$$

but $X_3 = P_3/P_3^0$

$$\therefore P_3 = P_t - P_n^0 (1-P_3/P_3^0)$$

$$P_3 P_3^0 = P_t P_3^0 - P_n^0 P_3^0 + P_3 P_n^0$$

$$P_3 P_3^0 - P_3 P_n^0 = P_t P_3^0 - P_n^0 P_3^0$$

$$P_3(P_3^0 - P_n^0) = P_t P_3^0 - P_n^0 P_3^0$$

$$P_3 = \frac{P_t P_3^0 - P_n^0 P_3^0}{P_3^0 - P_n^0} = \frac{P_3^0(P_t - P_n^0)}{P_3^0 - P_n^0}$$

given $\quad P_n = P_t - P_3$

then $\quad P_n = \dfrac{P_n^0 (P_t - P_3^0)}{P_n^0 - P_3^0}$

VAPOR PRESSURE vs. $\dfrac{1000}{T^0 K}$ (After Stull, 1947)

torr	C_3	C_6	C_7	Iso-C_8	C_9	C_{10}
1	6.93	4.56	4.18	4.22	3.63	3.45
5	6.34	4.19	3.83	3.87	3.34	3.17
10	6.07	4.03	3.69	3.72	3.21	3.04
20	5.81	3.86	3.54	3.56	3.08	2.92
40	5.53	3.69	3.38	3.40	2.95	2.80
60	5.37	3.59	3.29	3.31	2.88	2.72
100	5.17	3.46	3.18	3.19	2.78	2.62
200	4.88	3.28	3.01	3.02	2.65	2.49
400	4.60	3.10	2.85	2.84	2.50	2.36
760	4.33	2.93	2.69	2.69	2.37	2.24

n	$t\,^{\circ}C$	$\dfrac{1000}{T\,^{\circ}K}$	Pressure, in torr			
			P_3^{0}	P_n^{0}	P_3	P_n
6	17.4	3.44	7,400	108	469	101
7	43.0	3.16	15,000	108	458	112
i-8	46.1	3.13	16,000	135	439	131
9	40.2	3.19	14,000	11	559	10.6
10	38.5	3.21	13,000	4.1	566	3.9

$$P_n = \frac{P_n^{0}\,(P_3^{0} - P_t)}{P_3^{0} - P_n^{0}} \qquad\qquad P_t = 570 \text{ torr}$$

for n = 6 $\quad P_6 = \dfrac{108\,(7,400 - 570)}{7,400 - 108} = 101$ torr

$\qquad\qquad\quad P_3 = \qquad\qquad\qquad\qquad 469$ torr

for n = 7 $\quad P_7 = \dfrac{108\,(15,000 - 570)}{15,000 - 108} = 112$ torr

$\qquad\qquad\quad P_3 = \qquad\qquad\qquad\qquad 458$ torr

for n = 8 $\quad P_8 = \dfrac{135\,(16,000 - 570)}{16,000 - 135} = 131$ tcrr

$\qquad\qquad\quad P_3 = \qquad\qquad\qquad\qquad 439$ torr

for n = 9 $\quad P_9 = \dfrac{11(14,000 - 570)}{14,000 - 11} = 10.6$ torr

$\qquad\qquad\quad P_3 = \qquad\qquad\qquad\qquad 559$ torr

for n = 10 $\quad P_{10} = \dfrac{4.1(13,000 - 570)}{13,000 - 4.1} = 3.9$ torr

$\qquad\qquad\quad P_3 = \qquad\qquad\qquad\qquad 566$ torr

n	% Air	% Propane	% Test HC
6	25	$\frac{469}{760} \times 100 = 61.7$	$\frac{101}{760} \times 100 = 13.3$
7	25	$\frac{458}{760} \times 100 = 60.3$	$\frac{112}{760} \times 100 = 14.7$
8	25	$\frac{439}{760} \times 100 - 57.8$	$\frac{135}{750} \times 100 = 17.2$
9	25	$\frac{559}{760} \times 100 - 73.6$	$\frac{11}{760} \times 100 = 1.4$
10	25	$\frac{566}{760} \times 100 = 74.5$	$\frac{4.1}{760} \times 100 = 0.5$

PROPANE

Vapor Pressure, Torr

1000/T°K
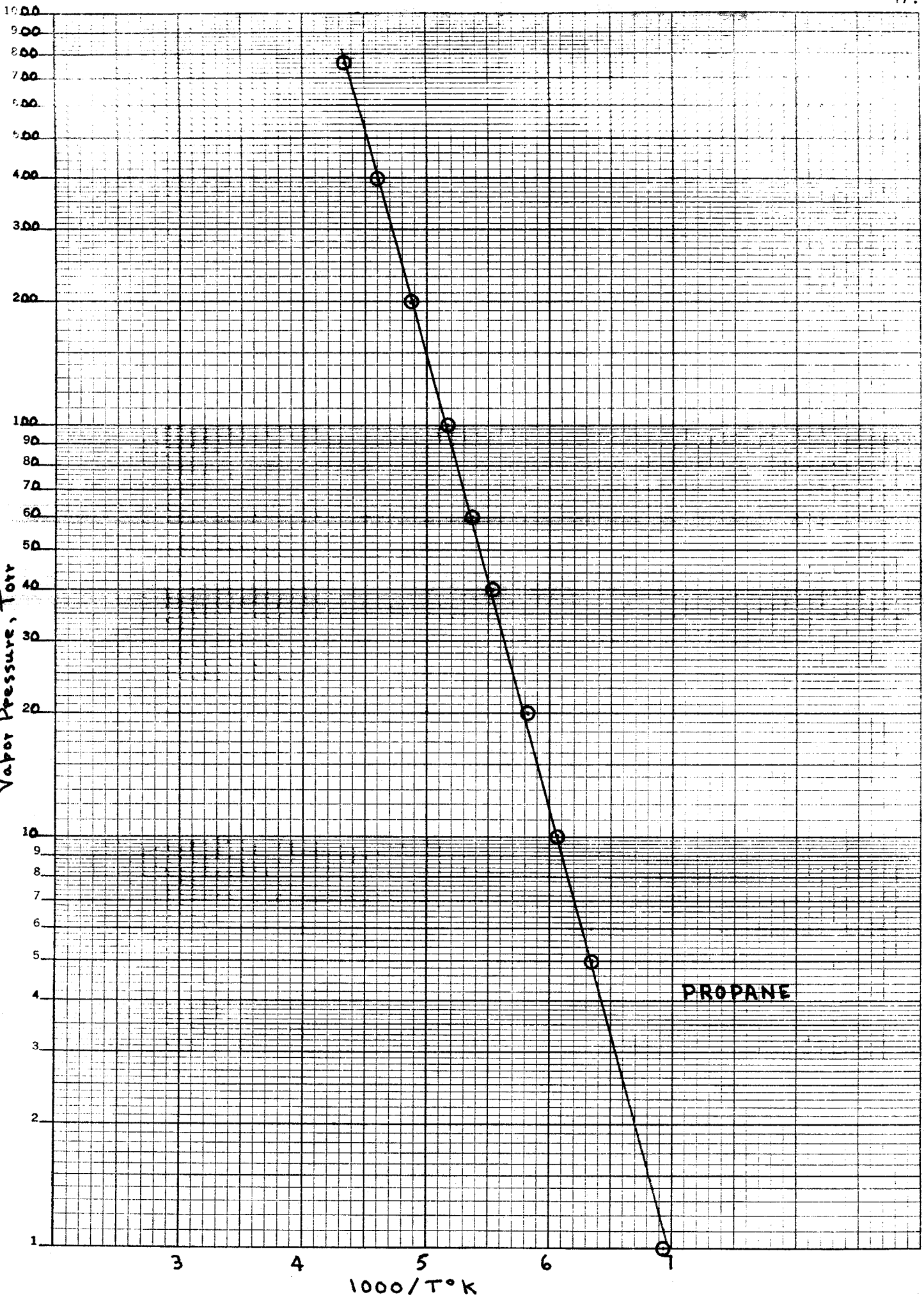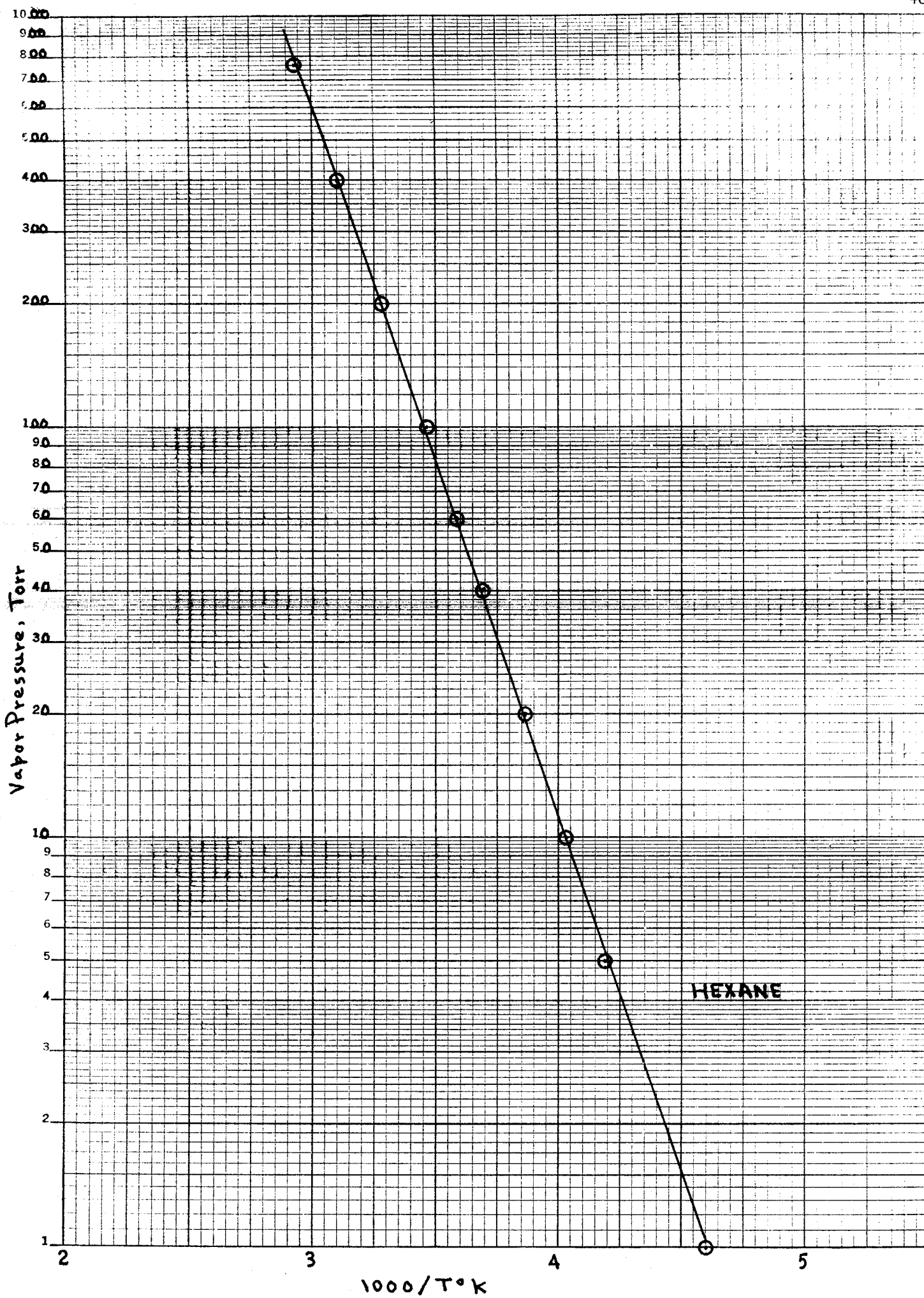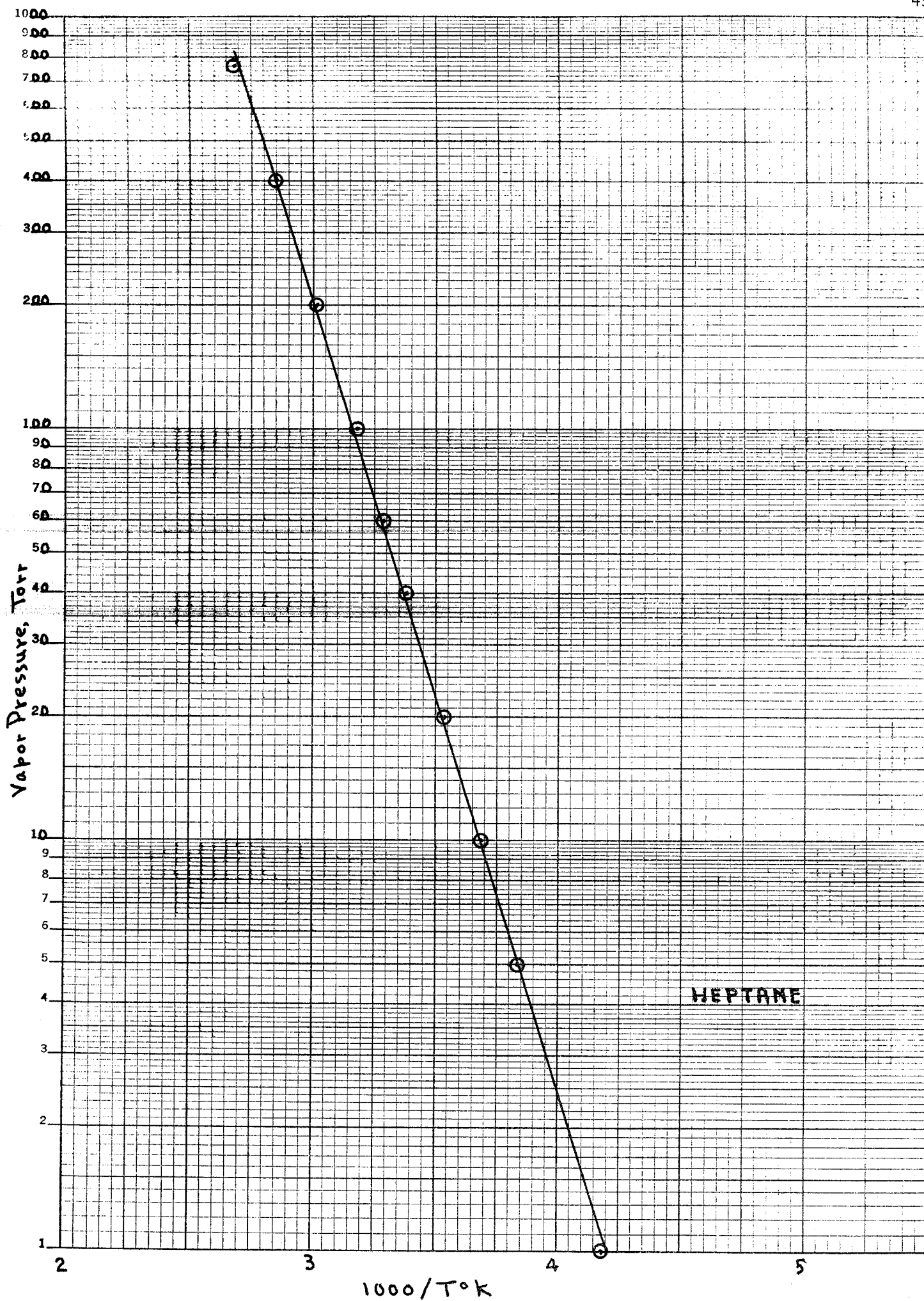
Vapor Pressure, Torr

SEMI-LOGARITHMIC   359-71
KEUFFEL & ESSER CO.   MADE IN U.S.A.
3 CYCLES X 70 DIVISIONS

HEXANE

1000/T°k

HEPTANE

i-OCTANE

Vapor Pressure, Torr

1000/T°K

SEMI-LOGARITHMIC   359-71
KEUFFEL & ESSER CO.   MADE IN U.S.A.
3 CYCLES X 70 DIVISIONS

NONANE

DECANE